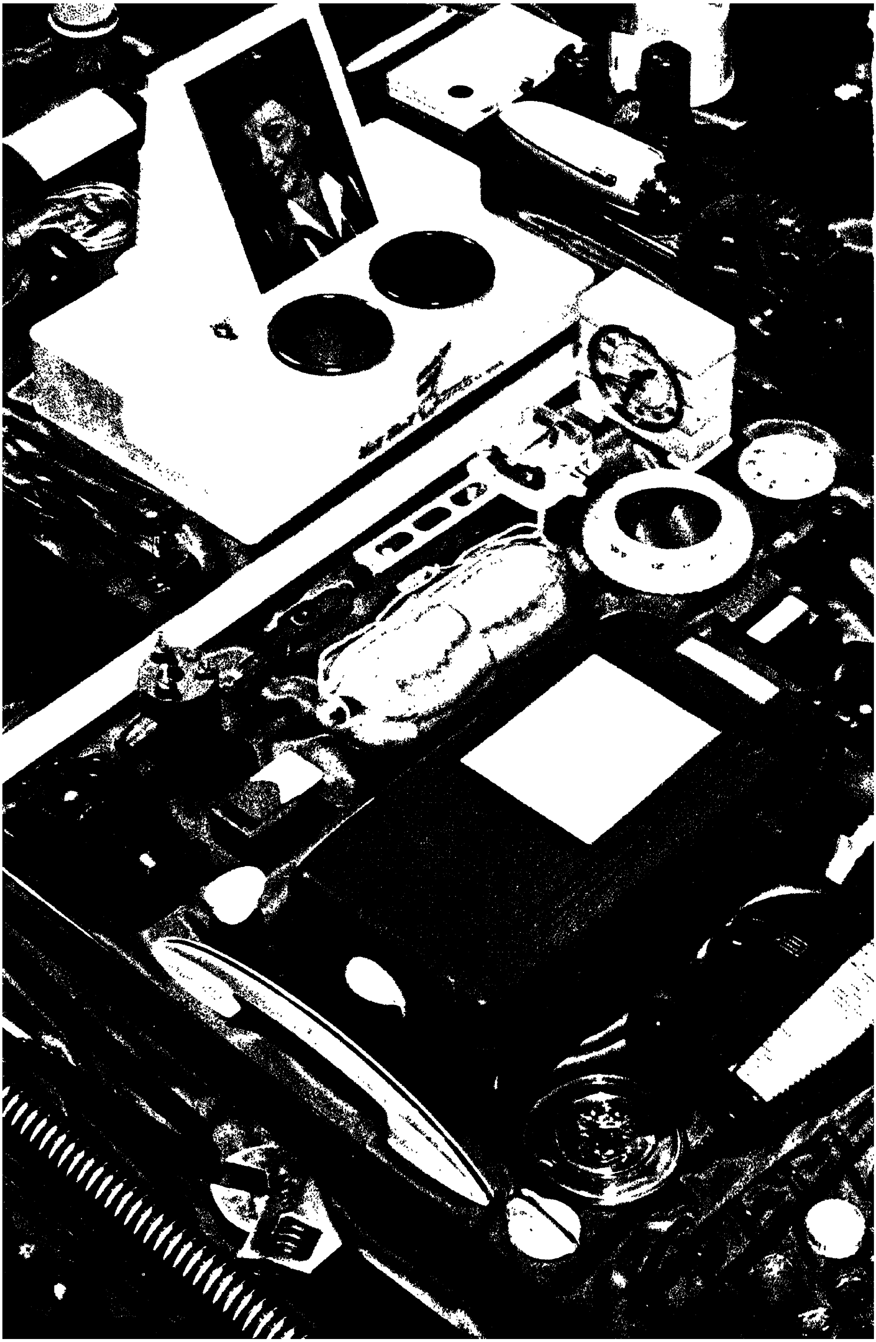

THE NEW PLASTICS

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PREFACE

early everyone interested in any branch of plastics is now asking it the new materials which have been hinted at from time to in the press. During the early war years the mother of invention to new heights with the result that a dozen or more new plastics appeared on the American scene and important improvements been made in a long list of the established materials.

uch else has happened during the last few years in the plastics in istry. New processes and new applications have appeared in profusion, and the production of so-called borderline materials, such as synthetic rubbers, organic coatings and adhesives has exceeded anything known in the past.

This book brings together for the first time information on all the important plastics materials developed since 1940 and, in addition, presents a roundup of important developments throughout the industry. It is, however, supplemental to earlier books on plastics rather than a new treatise on the subject as a whole. Yet for those who may not have the earlier books a condensed review of the industry is included in Chapter I. All the other chapters are devoted to happenings since 1940 and up to March, 1945.

Chemical diagrams of some of the more important new plastics are in the Appendix at the end of the book.

Concerning the new materials, information is still to some extent under government secrecy orders. However, it is hoped that the data available at this time covering these truly amazing new products will be of help, not only to those using plastics but to all who are working in the industry. Chapter XIII gives some comment on work still in the laboratory stage with suggestions as to what may be ahead.

H. R. S.
M. H. B.

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CONTENTS

INTRODUCTION

One of the new plastics is referred to as a steel-like material, another is rubber-like and still others resist acids, high temperatures and electrical currents to a degree not possible with previous plastics materials. It is difficult in fact to describe the new developments in this field without resorting to hyperbole, and with this in mind the authors have sought comments from a wide variety of authorities, hoping in this way to temper their own enthusiasm. Some of these comments are presented here.

"Despite phenomenal advances," says one research worker, "the ideal plastic is still some distance away. Nearly always improvement in physical properties is accompanied by increase in price." Another comment in the same vein points out that bettering one property may mean lessening another. Thus, greater hardness is likely to mean greater brittleness.

During the year 1944 plastics were much in the limelight. This may be good for the industry and it may be harmful. On this subject, John G. Rodabaugh[1] reports, "Many people have been led to expect more of plastics than will be forthcoming for many years. Much of the expansion that the industry has enjoyed recently has been due to shortages in other materials rather than to the fact that plastics do the job better or more economically. Plastics are not cheap and in most applications their use is indicated not because of the price per pound, but because of their light weight and ease of fabrication."

Much of the comment on recent plastics developments has stressed process rather than product. Typical of this is the report from George K. Scribner[2] which states, "I think the greatest recent development in the field of plastics is the introduction and improvement of electronic heating of molding preforms. By speeding up the

[1] Fiduciary Counsel, Inc.
[2] Boonton Molding Company.

cure, this has placed thermosetting compounds closer in cost of production to the thermoplastics. It has also increased quality to a degree not easily measured. By its use, higher speed means less expensive mold cavities for a given weekly output and also less rejects. It opens up the possibility of more complicated and larger pieces than heretofore and it permits the use of higher impact materials with almost the same freedom as previously with run-of-mine wood flour stock."

Those who commented on new materials have nearly all emphasized the "importance of nylon both as a fiber and as a molding powder."

Based on replies to inquiries, the materials developed during the last three or four years might be rated in probable importance as follows: nylon, melamine, vinylidene chloride, polyethylene, silicone, allyl and zein. Several others such as tetrafluorethylene and polyvinyl carbazole are not well enough known as yet even among research workers to give them a place in the rating.

The manner in which the new developments in the plastics industry have solved pressing problems is described in the comment of J. R. Townsend.[1] "The consumer of plastics," he writes, "had five major problems emphasized by the war. These were, (1) a need for a textile fiber which would be strong, elastic and water repellent; (2) a need for reduced press cycle time for thermosetting plastics; (3) a need for water and heat resisting adhesives to permit production of low pressure laminates; (4) the desire to secure thermoplastic materials capable of resisting boiling water without distortion; and (5) the demand for a rubber-like material without the defects of rubber."

"All of these problems," continues Mr. Townsend, "have been solved. Nylon is now so generally accepted as a super silk that it is hard to realize it was unknown previous to 1940. Aside from use as parachute cloth, clothing, rope or cordage, it has good electrical insulation properties. When extruded, it forms bristles or it may form flexible heat resistant tubing. As a solid molding material it is moisture and heat resistant.

[1] Bell Telephone Laboratories.

"Electronic heating reduces press cycle time to as low as 10 per cent of the time required with bulk powder and externally applied heat. Adhesives such as Cycleweld, Redux, melamine, phenol and urea formaldehyde open up new fields for the de-

Courtesy American Cyanamid Co.

FIG. 2. Plastics enter nearly every phase of the war program. This shows a melamine distributor housing on an aircraft motor.

signer. With these we can now have composite structures of wood, metal, rubber and leather, and further we can have low pressure laminates and formable composites. Wood, cast iron, ceramic and even concrete molds can now be used in place of expensive die steels. Compound curved sections can be formed by bag mold-

ing. Cycleweld is of particular significance since it provides, for the first time, means of holding metal and nonmetal parts together with strength rivaling that of riveting and welding. Allyl resins, new heat resistant methyl methacrylates and others permit fabrication of boilable medical and technical appliances. A variety of elastomeric or nonrigid plastics are available in such new materials as vinyl chlor acetate, vinyl butyral, vinyl alcohol and ethyl cellulose. These materials may be compounded to provide a tremendous range of properties."

The Army and Navy would have had great difficulty shipping machinery and supplies to the South Pacific without the protection against moisture afforded by some of the new packaging materials such as vinylidene chloride and waterproof cellophane. These and other new plastics have revolutionized the whole packaging industry, making it practical to ship such items as oil and molasses in bag containers.

The possibilities of the new plastics, despite all cautioning, seem limitless and the authors realize that this book is but a first step in the job of describing them.

CHAPTER I

Review of Industry up to 1940

To MAKE the following summary of the plastics industry up to 1940 clear, a few basic terms must be defined.

"Plastics," as used today, generally refers to organic chemical materials that are not found in nature but are of synthetic (man-made) origin. Two characteristics are common to all plastics: at some stage in production they can be shaped or cast, and they can be set in a more or less rigid condition.

One of the commonest ways of classifying plastics is to use the terms "thermosetting" and "thermoplastic."

Thermosetting means heat-hardening and refers to those plastics that become sufficiently soft on the *initial* application of heat and pressure in the mold to flow and fill out all the contours of the mold, but upon *further application of heat and pressure*, they "cure" or complete a chemical reaction to become a hard, infusible, inert molded piece, which cannot be resoftened by reapplication of heat.

Thermoplastic means heat-softening and refers to those plastics that become sufficiently soft on the application of heat and pressure in the mold to flow and fill out all the contours of the mold, and that, by *chilling the mold*, assume a rigid or semirigid form. No chemical reaction takes place, and the piece *can* be resoftened by reheating.

"Fillers" are added, if necessary, to synthetic resins (generally thermosetting) to modify properties of molding compounds. They are inert materials, commonly wood flour, asbestos, graphite, mica and paper.

"Plasticizers" are added to plastics (generally thermoplastic) to introduce new physical and thermal properties. They are often used to lower the melting point or to improve flow and plasticity. Some common plasticizers are camphor, castor oil, triphenyl phosphate and phthalates.

"Resin" and "plastic" are often used interchangeably. The chief distinguishing component, sometimes the only component, of a plastic is a synthetic resinous material. The resin is the material before processing and the plastic is the material after processing, a distinction not always observed.

The synthesis of plastics resins, or the compounding with fillers and plasticizers, is of interest chiefly to those who produce them. Of greater general interest is the handling of plastics for fabricating purposes. A brief outline of the most important primary methods of fabrication follows:

A. Well-Established Methods. The four well-established methods for fabricating plastics are:

Molding
Extruding
Casting
Laminating

There are many variations, but almost any operation can be classified under one of these processes.

1. *Molding.* This is by far the most widely used method of fabrication and can in turn be subdivided into the following modifications:
   (a) *Compression molding.* This method is used primarily for producing finished shapes or products from thermosetting materials. A molding compound, usually in the form of a dry powder or pressed preforms, is placed in a mold and subjected to heat and pressure until it has filled out the contours of the mold and has "set." The pressure is then released, the mold opened and the molded part ejected while hot. The chief advantage of the process is that parts so produced require little further processing. Thermoplastics are not generally molded by this method. They must be allowed to cold-set before ejecting from molds.
   (b) *Injection molding.* This is used to produce finished shapes or products from thermoplastic materials. The material is heated in a pressure cylinder, forced while hot through an orifice into a cold mold, allowed to cool for a few seconds and then automatically ejected from the mold. The process is adaptable to automatic operation. It has not been widely used for thermo-

setting materials because of complications in controlling the exact time of cure. The cost is low, however, and injection molding of thermosetting materials, such as the jet molding process, has been accomplished and is discussed later.

(c) *Transfer molding.* This method was developed to bring some of the advantages of injection molding to thermosetting materials. The charge is first heated in a central chamber and then is forced through small heated passages into the mold where additional heat and pressure complete the cure. This results in filling the mold more rapidly and reducing the curing time, thus shortening the molding cycle.

(d) *Blow molding.* This procedure is confined to thermoplastic materials. Thin sheets or tubes are softened by heat and placed in a closed mold. Compressed air, introduced between the sheets, forces the plastic to take the shape of the mold and thus to produce hollow articles such as the familiar celluloid toys.

2. *Extrusion.* This is confined chiefly to thermoplastics. Hot material is forced through a die in continuous strips, tubes or shapes. The die controls the shape of the extrusion, which hardens by air or water cooling as it leaves the die. This process, by its nature, is adaptable to stock materials such as strips, rods, or tubing, which can later be cut to length or processed further.
3. *Casting.* This differs from molding principally in that no pressure is used. Resins are poured into molds in a liquid form and cured later by heat or catalyst action. Because there is no pressure, inexpensive molds made of such soft materials as lead or zinc can be used. In general, casting is used for stock materials in the form of sheets, rods, tubes and films that can be fabricated later as desired. Molding dominates the field of finished articles or parts, but some special shapes are cast to take advantage of the low cost of molds.
4. *Laminating.* This process usually involves drawing a roll of material (paper, fabric, etc.) through an impregnating tank containing a liquid resin compound known as a varnish. After impregnating the material is passed slowly through a drying oven, where heat effects a partial cure. The dry material is cut into sheets, pressed and heated to cure or rolled on mandrels to form tubing. The process for making plywood is similar except that veneers of wood are treated with the varnish by dipping, spraying or brushing, or sheets of plastic may be interposed between plywood layers.

B. MORE RECENT METHODS. Among the more recent methods of fabricating plastics are the *fluid pressure bag-molding process* and the *pulp preform process.*

1. *Fluid pressure bag-molding process.* This method has undergone intensive development in recent years, and structures as large as half an airplane fuselage can now be molded in a single piece. One process is the Vidal method, best known in airplane manufacture. A wood male mold is used and the sheets of veneer spread with resin adhesive are built up on it. The entire assembly is then placed in a rubber bag and a vacuum is drawn. This causes the bag to adhere to the mold like a rubber glove, forcing the sheets to conform to the shape of the mold. A pressure tank, where steam and hot air are applied, completes the cure. Only low pressures and temperatures are required. In another process known as Duramold, the veneer is laid in a female mold and pressed with an inflated bag. There are various modifications of these processes.
2. *Pulp preform process.* Essentially this consists in building preforms of the finished part. A resin is mixed with fibers in a pulp state, the resinous pulp is lifted from the solution by a screen in the form of the part desired and vacuum then draws off the water and forces the pulp to assume the shape of the screen. The preform, which is three or four times the thickness of the finished piece, is then dried and transferred to a hydraulic press for the molding process.

C. SECONDARY FABRICATING. There are many other methods of handling plastics that are generally referred to as fabricating methods, because they are used to process materials that have already been molded, cast, laminated or coated. Most of these operations are self-explanatory. They include the following methods, one or more of which may be used in handling plastics:

1. Sawing	11. Beveling
2. Drilling	12. Polishing
3. Turning	13. Tapping and threading
4. Punching	14. Fastening and joining (bolting, cementing, etc.)
5. Milling	
6. Shearing	15. Embossing, engraving and etching
7. Machining	
8. Drawing	16. Forming and bending
9. Planing	17. Carving
10. Grinding	18. Plating

COMMERCIAL FORMS

The forms of plastics materials offered for sale are as follows:

A. AVAILABLE FROM FABRICATORS

1. *Finished products or parts.* These may be one of the following:
   (a) Molded products
   (b) Cast shapes
   (c) Fabricated articles (formed and assembled from molded, cast, laminated and coated materials or from stock materials)

B. AVAILABLE FROM FABRICATORS AND/OR RAW-MATERIAL SOURCES

1. *Stock materials.* Sheets, rods, tubes, strips, filaments, strands, films and foils made by molding, casting, laminating or coating.
2. *Glues, adhesives and sealing compounds.* Many plastics materials can be used in an adhesive capacity without the heat and pressure essential to lamination.

C. AVAILABLE FROM RAW-MATERIAL SOURCES

1. *Molding compounds*
2. *Casting resins*
3. *Laminating resins*
4. *Coating compositions*

SCOPE OF USES

Although most people think of plastics as molded articles, they are, of course, used in many other ways. The use of resins in coatings illustrates the diversity of plastics applications. Coatings range from textile treatments to corrosion-resistant industrial finishes for metals. Their utility is continually increasing in waterproofing textiles, in producing crush-resistant materials and in improving the abrasion resistance of fabrics. They are also important in the paint, varnish, baked-on enamel and lacquer fields.

Laminates range from flexible sheets to materials rivaling steel in strength-weight characteristics. Synthetic resin adhesives have been used to laminate almost anything available in sheet form — even thin sheets of metal have been successfully laminated.

The packaging field makes use of plastics films such as cellophane, ethyl cellulose, and vinylidene chloride.

Radio cabinets, automobile handles, hardware novelties and

electrical housings are among the best known applications, misjudged by many to represent the whole field. The term plastics, however, does not refer to a single type of material any more than the term metal does. The individual materials and their specific qualifications for a particular job should be considered and the various types of plastics distinguished just like steel and copper and lead and tin. The following paragraphs review the principal types of plastics in use prior to 1940.

IMPORTANT PREWAR PLASTICS

A. THERMOSETTING

1. *Phenolics (phenol-formaldehyde and phenol-furfural).* Broadly, the term phenolics includes not only the phenol-formaldehyde and phenol-furfural resins, but also certain other resins of coal-tar origin, such as those made from cresol. The most important members of the group are produced by the reaction of phenol with an aldehyde such as formaldehyde or furfural.

The phenolics are one of the oldest and most widely used of all plastics and are often referred to as the "workhorse" of the industry. They are dimensionally stable, that is, they do not creep, warp or change shape under varying temperature and humidity conditions. This property accounts for their wide usage in such functional items as pump parts, automotive and aircraft parts, industrial valves and mechanical parts. They also have excellent resistance to solvents and oils.

Specific properties can be imparted to phenolics by blending the resin with a wide variety of fillers. Fabric or cord fillers yield phenolics with high mechanical strength, mica fillers give high electrical insulation and asbestos results in high heat resistance.

The chief lack in phenolics is stable color range — they are confined (except cast phenolics) to dark, opaque or highly pigmented colors.

Phenolics are available in the following forms for further processing:

Molding compounds
Casting resins
Cast shapes
Liquid resins

Dry resins
Laminated sheets, rods and tubes

Primary methods of fabrication include the following:
Compression molding
Transfer molding
Casting
Laminating
New specialized processes

Secondary methods of fabrication are machining of cast shapes and machining of laminates.

Generally speaking, their specific properties might be summed up as follows:

Dimensional stability	Excellent
Solvent and oil resistance	Excellent
Thermal stability	Excellent
Water resistance	Good

Properties may be varied through the use of fillers as follows:

General purpose	Wood flour filled
Heat resistance	Asbestos filled
Electric insulation	Mica filled
Impact materials	Fiber, fabric and cord filled

Some of the principal producers of phenolic molding compounds, with trade names:

Bakelite Corporation	Bakelite
Catalin Corporation	Catalin
Durez Plastics & Chemical Company	Durez
Durite Plastics	Durite
General Electric Company	Textolite
A. Knoedler Company	Gemstone
Makalot Corporation	Makalot
Marblette Corporation	Marblette
Monsanto Chemical Company	Resinox, Opalon
Reilly Tar & Chemical Company	Indur
Resinous Products & Chemical Company	Amberol

Important producers of laminated sheets, rods and tubes:

Columbian Rope Company	Co-ro-lite
Continental-Diamond Fibre Company	Cellanite, Dilecto
Farley & Loetscher Manufacturing Company	Farlite
The Formica Insulation Company	Formica

General Electric Co.	Textolite
Keyes Fibre Company	Kys-Ite
Mica Insulator Company	Lamicoid
National Vulcanized Fibre Company	Phenolite
Panelyte Corporation	Panelyte
The Richardson Company	Insurok
Synthane Corporation	Synthane
Taylor Fibre Company	Taylor
Westinghouse Electric & Mfg. Company	Micarta

2. *Ureas (urea-formaldehyde).* In the thermosetting field the ureas supply the decorative beauty and range of color lacking in phenolics.

In other properties, however, they are similar to the phenolics and consequently find chief application in functional parts in which appearance is a factor, in electrical fixtures, stove handles, table and counter tops.

Urea-formaldehyde is produced by the reaction of urea, a nitrogen compound, with formaldehyde. The ureas are not adapted to blending with a wide variety of fillers and therefore are not so versatile as the phenolics.

The following forms of ureas are available for further processing:

Molding compounds
Impregnating resins
Surface coatings
Adhesives

Primary methods of fabrication are:

Compression molding
Laminating
Hot and cold bonding of plywoods and fabrics
New specialized processes

In general, the ureas have the following properties:

Translucency	Excellent
Alcohol, oil and grease resistance	Excellent
Electrical properties	Very good to excellent
Thermal stability	Very good
Mild acid and alkali resistance	Very good
Dimensional stability	Very good
Moisture or humidity resistance	Good
Color range (light fast)	Complete
Odorless and tasteless	

Some of the principal producers and trade names are:

American Cyanamid Company	Beetle
Bakelite Corporation	Bakelite Urea
Plaskon Division	Plaskon
Resinous Products & Chemical Company	Uformite

B. THERMOPLASTIC

1. *Cellulose acetate and cellulose acetate butyrate.* Cellulose acetates are among the oldest and the best known of the moldable thermoplastic resins.

Their toughness, particularly in thin sections, as well as their ease of fabrication and complete color range, have resulted in wide usage in decorative parts, articles and trim. They have been used especially in containers, housings, cases, costume jewelry and novelties, where resistance to high humidity and to temperatures not over 150°F. is not required. The acetate butyrates and high-acetyl acetates are considerably more stable to elevated temperatures and humidities than the straight acetates and have greatly broadened the field of application.

Cellulose acetate is produced by treating cotton linters or wood pulp with acetic acid and acetic anhydride. The degree of acetylation can be controlled, and both low- and high-acetyl acetates are available. Cellulose acetate butyrate is made by treating cotton linters with a mixture of acetic and butyric acids and anhydrides.

The cellulose acetate materials are available in the following forms for further processing:

Molding compounds
Sheets and films
Rods and tubes
Pressed blocks
Stock moldings

The primary methods of fabrication are:

Injection molding
Extrusion
Laminating
Blow molding

The secondary methods of fabrication are:

Shaping and forming with heat
Machining
Heat bonding or cementing with acetone

Drawing
Stamping
Embossing, engraving and etching

These materials have the following properties:

	Cellulose Acetate	*High Acetyl and Acetate Butyrate*
Fabricating versatility	Excellent	Excellent
Colorability	Complete	Complete
Toughness	Very good	Very good
Transparency	Very good	Very good
Dielectric strength	Very good	Very good
Moisture or humidity resistance	Fair	Very good
Dimensional stability	Fair	Very good

Some of the most important producers and trade names are:

Bakelite Corporation	Bakelite Acetate
Celanese Plastics Corporation	Lumarith
E. I. du Pont de Nemours & Company, Inc.	Plastacele
Hercules Powder Company	Hercules Acetate
Monsanto Chemical Company	Fibestos
Nixon Nitration Works	Nixonite
Tennessee Eastman Corporation	Tenite I, Tenite II

2. *Cellulose Nitrate.* Cellulose nitrate under the trade name Celluloid was the original thermoplastic material. It is tougher than cellulose acetate and comparable in decorative beauty. It has been widely used in such things as brush and mirror backs, baby rattles, ping-pong balls, pen and pencil barrels, chisel and screw driver handles and mallet heads.

Its serious drawback is its inflammability. It cannot be molded by usual methods or used for any purpose where flames or even high temperatures may be encountered.

Cellulose nitrate is produced by treating cotton linters with nitric acids. It is available in the following forms for further processing:

Sheets, rods and tubes
Extruded shapes

Primary methods of fabrication are:

Wet extrusion
Casting
Laminating

Secondary methods of fabrication are:
- Machining
- Stamping
- Embossing, engraving, printing
- Drawing
- Wet heat forming
- Stitching, riveting, cementing

Cellulose nitrate has the following properties:

Toughness	Excellent
Ease of printing and fabricating	Excellent
Colorability and ability to take color designs	Complete
Moisture or humidity resistance	Very good
Transparency	Excellent
Dimensional stability	Fair to good
Burning rate	Very rapid

Some of the important producers and trade names are:

Celanese Plastics Corporation	Celluloid
E. I. du Pont de Nemours & Company, Inc.	Pyralin
Monsanto Chemical Company	Nitron
Nixon Nitration Works	Nixonoid

3. *Ethyl Cellulose.* Ethyl cellulose is the newest of the cellulose plastics and is characterized by exceptional toughness and flexibility, both of which are retained at below zero temperatures. It has outstanding resistance to alkalies and weak acids, good resistance to moisture, good dimensional stability, and is a good electrical insulator.

Its chief uses prior to the war were as transparent packages formed from sheet and as extruded wire insulation. Its low-temperature toughness, electrical insulation and dimensional stability have resulted in important uses in war applications.

Ethyl cellulose is obtained by treating cotton linters with caustic soda and ethyl chloride. It is available in the following forms for further processing:
- Molding compounds
- Sheets, rods and tubes

Primary methods of fabrication are:
- Injection molding
- Extrusion molding
- Compression molding (used infrequently)
- Laminating

Secondary methods of fabrication are:
- Machining
- Heat forming
- Drawing, stamping
- Embossing, engraving, printing
- Cementing, heat bonding

Ethyl cellulose has the following properties:

Toughness at below 0°F temperatures	Excellent
Dielectric strength	Excellent
Colorability	Complete
Moisture or humidity resistance	Good
Aging resistance	Very good
Dimensional stability	Good
Transparency	Very good

Some of the important producers and trade names are:

Celanese Plastics Company	Lumarith E C
	Lumarith E R
Dow Chemical Company	Ethocel

4. *Acrylics — Methyl Methacrylates.* The acrylics are familiar in the form of transparent brush backs and bomber turrets. The prewar uses ranged from artificial teeth, novelty jewelry, lenses, dials and bezels through edge-lighted outdoor signs and large transparent working models and mechanisms. Their clarity, dimensional stability, weather resistance and lightness adapt them for all types of airplane windows. Methyl methacrylate is synthesized by treating propylene, a petroleum derivative, with acetone and methyl alcohol.

The acrylics are available for further processing in the following forms:
- Molding compounds
- Sheets, rods and tubes
- Castings

Primary methods of fabrication are:
- Injection molding
- Extrusion molding
- Compression molding

Secondary methods of fabrication are:
- Heat forming

Machining
Drawing and stamping
Acrylics have the following properties:

Edge lighting	Unique
Transparency	Excellent
Dimensional stability	Excellent
Weather resistance	Excellent
Colorability	Complete
Humidity resistance	Very good
Dielectric strength	Very good

Some of the important producers and trade names are:

E. I. du Pont de Nemours & Company, Inc.	Lucite
Rohm and Haas	Plexiglas

5. *Styrene* (*Polystyrene*). This material has been widely used in electrical and radio parts because of its near perfect electrical insulation properties and its almost complete water resistance. Its resistance to acids and alkalies, oils and solvents, combined with extremely light weight and good dimensional stability, have led to wide applications in containers, closures, refrigerator parts, radio parts, instrument panels, colored light reflectors and tableware.

Polystyrene is synthesized from benzene and ethyl chloride. It is available for further processing in the following forms:
Molding compounds
Sheets, rods and tubes
Primary methods of fabrication are:
Injection molding
Extrusion
Compression molding
Secondary methods of fabrication are:
Heat forming
Machining

Polystyrene has the following properties:

Dielectric properties	Excellent
Moisture or humidity resistance	Excellent
Dimensional stability	Excellent
Colorability	Complete
Acid and alkali resistance	Excellent
Transparency	Very good

Some of the important producers and trade names are:

Bakelite Corporation	Bakelite polystyrene
Catalin Corporation	Loalin
Dow Chemical Company	Styron
Monsanto Chemical Company	Lustron

6. *Polyvinyl Chloride.* This has been available for use only as a plasticized flexible material. Its outstanding resistance to water, concentrated acids, alkalies and alcohols as well as its durability have resulted in industrial uses such as cable coverings and tank linings and as extruded electrical wire covering for low-voltage lines and telephone wires. In addition to the above properties, its transparency and toughness have made polyvinyl chloride a satisfactory material for rainwear, shower curtains and aprons.

Vinyl chloride is produced by reacting acetylene gas with dry hydrogen chloride. Polymerization results in the formation of polyvinyl chloride.

Polyvinyl chloride is available in the following forms for further processing:

Milled batch stock for extruding
Flexible sheet and film
Flexible rods and tubing
Polyvinyl chloride resin
Sponge

Primary methods of fabrication are:

Extrusion
Compression molding
Special casting
Laminating
Calendering

Secondary methods of fabrication are:

Heat forming
Heat bonding or cementing

Polyvinyl chloride has the following properties:

Electrical insulation	Excellent
Resistance to oil, chemicals, water and gasoline	Excellent
Resistance to aging (weather and sunlight)	Excellent
Flexibility at low temperatures	Very good
Color range	Complete
Fire resistance	Will not propagate flame

Some of the important producers and trade names are:

Carbide and Carbon Chemicals Corporation..	Vinylite P C (Unplasticized flake)
B. F. Goodrich Company..................	Geon

7. *Polyvinyl Acetate.* This resin has found wide use because of its excellent adhesive properties. Moreover, it is odorless, tasteless, nontoxic and colorless. It can either coat the surface that is to be bonded or it can be used as a thin tape interliner of the resin and bonded with the aid of heat. It is also useful in connection with latex emulsions or as an ingredient of pressure-sensitive adhesives.

Its resistance to water, aging and to action by fats and oils has resulted in its wide use as a paper coating material in the manufacture of such articles as paper drinking cups, oil containers and food packagings.

When liberally compounded with fillers such as wood flour, polyvinyl acetate can be shaped or molded into many attractive decorative articles such as plaques.

Polyvinyl acetate is formed by the polymerization of vinyl acetate obtained from the reaction of acetylene gas with acetic acid. It is available in the following forms for further processing:

- Solutions
- Dry resins
- Bonding tape (heat sealing)
- Emulsions

Primary methods of fabrication are:

- Use in an adhesive capacity
- Coating (as a solution treatment for leather, textiles, felts, straw, etc.)
- Compression molding (heavily filled with wood flour makes moldable plastic wood)

Polyvinyl acetate has the following properties:

Adhesive strength and versatility...........	Excellent
Water, oil and fat resistance................	Very good
Aging resistance..........................	Very good
Burning rate..............................	Very slow
Odorless, tasteless, nontoxic	

Important producers and trade names are:

Carbide and Carbon Chemicals Corporation..	Vinylite P A
E. I. du Pont de Nemours & Company, Inc.	Butacite

8. *Copolymers of vinyl chloride and vinyl acetate.* These are often referred to as "copolymer vinyls" and are obtained when vinyl chloride and vinyl acetate are mixed and copolymerized.

The material is noteworthy for its resistance to water, alcohols, alkalies, mineral acids and solvents, and for its durability. It has excellent electrical properties and is widely used as extruded flexible wire coatings and other electrical insulations. It may be compounded with fillers, plasticizers and pigments to produce attractive rigid and flexible products. Rigid types have been used in items that must be dimensionally stable, such as dials, instruments, escutcheons, shatter-resistant windows and book bindings. Flexible types have been used in coated fabrics, raincoats, shower curtains, suspenders, belts and furniture upholstery.

Molded products of both rigid and flexible nature had not gained wide acceptance before the war primarily because plated molds and more rigid molding controls were required. However, considerably more experience has been gained in war applications, and after the war more molders should find the material useful. It is available for further processing in the following forms:

- Molding compounds
- Rigid sheets
- Flexible sheet and film
- Coated paper
- Dry resins for surface coating

Primary methods of fabrication are:

- Injection molding
- Extrusion molding
- Compression molding
- Solution coating
- Calendering
- Laminating

Secondary methods of fabrication are:

- Heat forming and drawing
- Stamping and swaging
- Heat bonding, cementing and stitching
- Embossing and printing

Copolymer vinyl has the following properties:

	Rigid	*Flexible*
Alcohol, acid, alkali, fats and mineral oil resistance	Excellent	Excellent
Dimensional stability	Excellent	
Moisture and humidity resistance	Excellent	Excellent
Electrical insulation	Excellent	Very good to Excellent
Aging resistance (sunlight)	Excellent	Very good
Color range	Complete	Complete
Flexibility at low temperatures		Very good to Excellent
Fire resistance	Will not support combustion	Dependent on type of plasticizer

Only producer and trade name is:

Carbide and Carbon Chemicals Corporation.. Vinylite

9. *Polyvinyl Butyral.* This was originally a one-purpose plastic and was used as the flexible interlining for safety glass. This material, however, has found many new war applications as a rubber substitute and is discussed in Chapter III.
10. *Chemurgic Plastics Materials or Agricultural Waste Plastics Materials.* Lignin and soybean plastics have received much publicity recently as substitutes capable of furnishing noncritical moldable plastics materials. However, the facts are that to date such materials have not been entirely satisfactory, with the exception of those pressed into sheets such as the well-known Masonite board and the lesser known Marathon board.

There is sufficient evidence now and some practical applications to prove that these materials reinforced with phenol-formaldehyde or other thermosetting resins are potentially sound and economical molding materials.

The lignin or soybean supply part or all the filler as well as a part of the resin; consequently, they are not capable of wide compounding with different fillers. In general, their properties are comparable to the general purpose, wood flour filled phenolics, which are the most widely used of the phenolics.

For all uses not requiring certain specific properties, these new materials of waste product origin are potentially economical and

should fit into a great many applications not reached in the past because of the basic cost of materials. It is entirely possible that this inexpensive plastic (with its inherent limitations) may be not too far distant.

(a) *Lignocelluloses* (*Lignin*). Lignocellulose plastics have been prepared from a variety of products including sawdust, wood chips, sugar cane (bagasse), corn stalks and other waste farm residues. The product is first treated with steam, washed, shredded and dried. After drying the resultant material is either pressed into sheets, rods and tubes, or mixed with phenol-formaldehyde or other thermosetting resins to form compression-molding compounds.

Forms available for further processing are:

Molding compounds (with reinforcing resins)

Laminated sheets, rods and tubes (straight)

Primary methods of fabrication are:

Compression molding

Machining of laminated parts

Specific properties are:

Laminated sheets, rods and tubes	
Mechanical strength	Good
Dimensional stability	Very good
Resistance to oils and solvents	Very good
Moisture and humidity resistance	Good to very good
Thermal stability	Good
Colorability	Black and brown only

The properties of resin reinforced molding compounds compare favorably with general purpose phenolics.

Some of the important producers and trade names are:

Burgess Cellulose (hardwood)	
Marathon Chemical Company (hardwood)	Marathon
Masonite Corporation (hardwood)	Masonite Bentolite
Paterson Plastics (softwood)	
Sheller Manufacturing Company (redwood)	Shellerite
Vulcanized Rubber Company (redwood)	Col-mor-lite
Valentine Sugars through Wolf and Company, Inc. (bagasse)	Valite

(b) *Soybean Base.* Oil-extracted soybean meal is mixed with phenol-formaldehyde, fillers, dyes, etc., to form molding compounds.

Forms available for further processing are:

Molding compounds

Primary method of fabrication is:

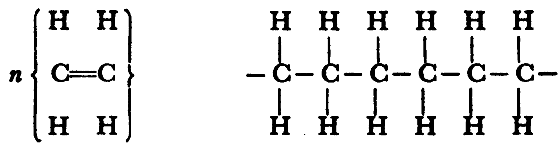
Compression molding

CHAPTER II

Most Recent Developments

POLYETHYLENE

POLYTHENE is the name given one group of polyethylene thermoplastics, originated by Imperial Chemical Industries, Ltd., of Great Britain and developed in this country by E. I. du Pont de Nemours & Company, Inc. Other polyethylene materials are produced by Carbide and Carbon Chemicals Corporation. The polyethylenes are hydrocarbon resins resulting from the polymerization of ethylene:



Ethylene Polyethylene

In the uncompounded state, the polyethylenes have a waxy white translucent appearance. They may be made transparent in thin sections, however, by proper quenching.

Outstanding properties include flexibility and toughness over a wide range of temperatures, unusually good resistance to water and to penetration by moisture, chemical inertness and unique electrical properties. Polyethylene is one of the lightest of all plastics, having a specific gravity of 0.92 to 0.93 at 20°C.

Polyethylene can be readily molded by injection or by compression, or extruded as sheets, films, fibers, tubes and other forms. It has a crystalline structure and in extruded form can be oriented by cold-drawing, with a resultant large increase in tensile strength. When deposited as a coating by hot-spraying or from solutions, it will form coatings that are waterproof and also inert to a wide variety of chemical agents.

Injection-molded standard Izod test specimens withstand a 2 ft-

lb. impact. At −49°F. strips 0.075 in. thick are not broken by a sharp bend. Water absorption in the standard A.S.T.M. test is 0.075 per cent. Transmission of water vapor is low. It is 0.4 gram for sheeting 0.004 in. thick and 0.07 gram for sheeting 0.010 in. thick per square meter over a 24-hr. period at 77°F.

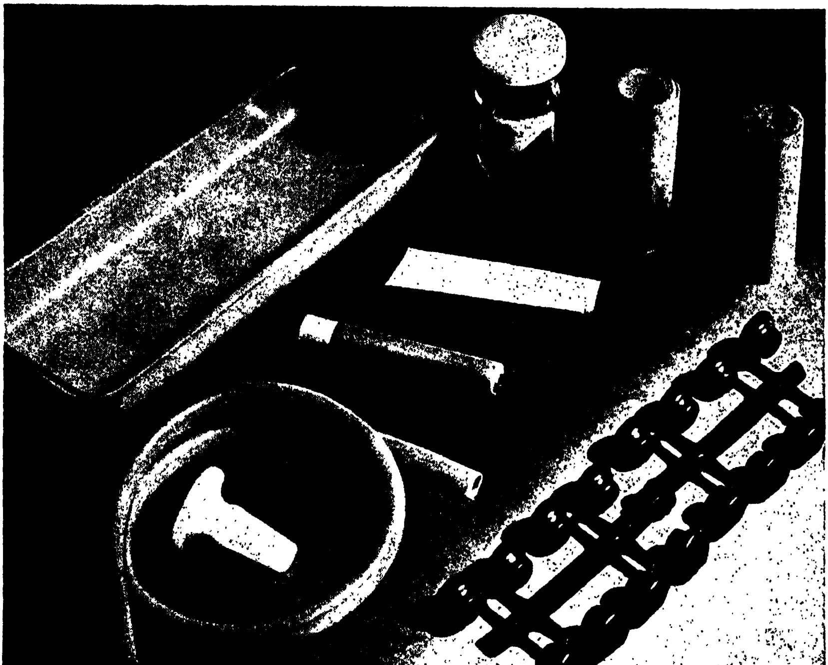
Courtesy Carbide and Carbon Chemicals Corp.

Fig. 3. Polyethylene resins are tough, horny, translucent materials.

Polyethylene occupies a peculiar place among plastics because of its modulus of rigidity. In thin sections, it may be classified as nonrigid, yet it lacks the limp rubbery quality that distinguishes most nonrigid plastics. Thick specimens, however, exhibit sufficient stiffness to warrant classification of the material among the more rigid plastics.

Possible future uses for polyethylene may include various types of containers, such as collapsible tubes for foods, drugs and cosmetics; gaskets and battery parts; flexible tubing or more rigid piping; waterproof and chemically resistant coatings; wire and cable insulation; adhesives; and films and sheets.

British experience in molding polyethylene indicates that two properties should be kept in mind. "First, an over-all contraction of 16 per cent occurs on cooling from the solidification to room temperature and for this reason, the pressure must be kept up on the molding during this period or voids and bubbles may be formed.



Courtesy E. I. du Pont de Nemours & Co., Inc.

FIG. 4. Resistance to many acids and alkalies plus extrusion characteristics give polythene a distinct field of application.

Secondly, the thermal conductivity is low so that large sections cool down quite slowly."[1]

Dr. J. W. Shackleton of E. I. du Pont de Nemours & Company, Inc., makes the following comment regarding the processing of polythene:

[1] *British Plastics*, December, 1943.

The extrusion of polythene involves no special difficulty when suitable equipment is available and reasonable attention is given to control. Illustrative of the technique is the procedure developed for covering wire with unplasticized polythene to make a quarter-inch cable. For this purpose it is best to use an extrusion machine of the type employed with plastics. The wire is preheated and fed at a uniform rate. The polythene in granular form is fed cold into the screw which may be cooled with water if necessary. Screens at the breaker-plate prevent the passage of lumps. The temperature of the throat, head and die are carefully controlled, for example, by circulation of oil. The freshly extruded material is cooled slowly, first in hot water and then in cold water. This slow cooling is required because of the extremely high coefficient of thermal expansion of polythene. The decrease of volume in cooling from 248° to 68°F. is approximately 12.5 per cent, and more than half of this takes place during a rapid crystallization between 248° and 176°F. Too rapid cooling would cause the surface of the coating to be hardened while the center remains still soft. The decrease in volume during further cooling would result then in the formation of voids in the interior of the mass. Mixtures of polythene with polyisobutylene can be extruded similarly and with less care in the cooling because the exterior does not become so rigid when cooled.

Polythene can be successfully molded by compression in positive molds. The thermal shrinkage is large. Hence it is particularly important to hold the molding under full pressure during the cooling, and desirable to cool relatively slowly in order to minimize the development of strains in the article. To make sound moldings, the material should be heated to at least 250°F., but temperatures above 320°F. should be avoided because they cause the article to adhere to the mold. An external lubricant may be applied to the surface of the mold to facilitate the removal of the molded article.

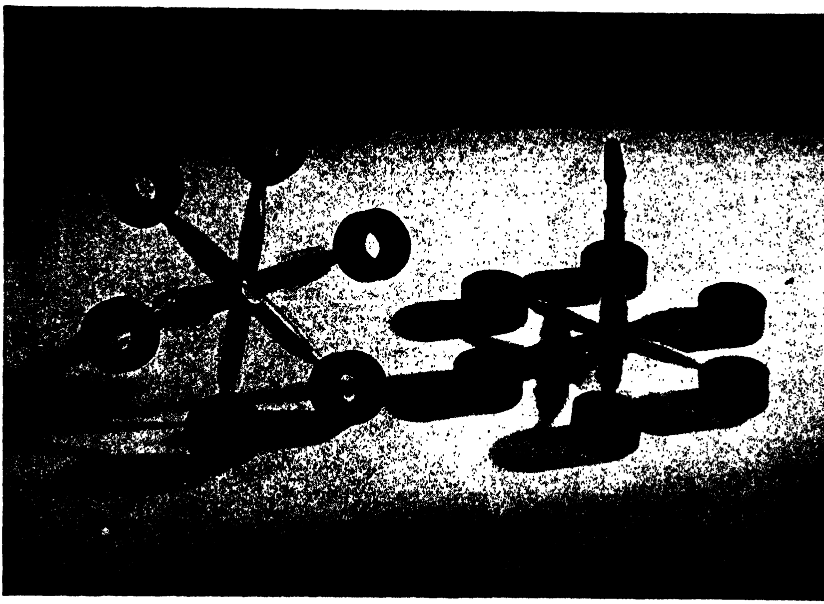
Polythene can be handled also in standard automatic injection-molding equipment with cylinder temperatures of 350° to 500°F., and die temperatures usually in the vicinity of 140°F.

Sheeting of polythene in various thicknesses can be made by calendering, by extrusion or by forming a block attached to a bedplate and slicing it as is done in the manufacture of the pyroxylin plastics. Massive polythene is readily machined with wood- or metalworking tools.

Waterproof and chemically resistant coatings of polythene can be applied from hot solutions of the resin, in, for example, xylene, or from dispersions in water or organic solvents, or by flame-spraying or "hot-melt" technique. A solution in xylene should be prepared at a temperature of at least 176°F., preferably 212°F. or more, and should be kept hot during its application. A film applied from

solution or dispersion should be either dried at a temperature above 212°F. or fused after it has been dried, to ensure a continuous and adherent film.

Films of polythene can be joined readily by heat-sealing, and massive polythene can be welded satisfactorily if care is taken to prevent excessive oxidation. For patching and welding, a mixture



Courtesy Carbide and Carbon Chemicals Corp.

FIG. 5. Standard injection molding methods are applicable to polyethylene resins.

of polythene with polyisobutylene is more satisfactory than polythene alone.

Polythene may be used either alone or compounded with other materials to modify its characteristics. Rigidity may be reduced by use of polyisobutylene, for example. Alone or compounded with waxes, it has excellent properties as an adhesive.

Production of polythene in commercial quantities was first announced by the du Pont Company in January, 1944, but the material was available in substantial quantities only by specific allocation for war purposes. Supplies of polythene previously available

TYPICAL PROPERTIES OF POLYTHENE

(Data given herein represent standard commercial grades of material and standard methods of testing except where otherwise noted.)

Property	Test Result	Test Method
Specific gravity..................	0.92	D71–27
Tensile strength, 70, 77, 170°F, psi	5000, 1700, 700 (1)	D638–42T (2)
Elongation, 77°F, %	30–500 (1)	D638–42T (2)
Modulus of elasticity, 77°F, psi	14,600 (1)	D638–42T
Flexural strength, 77°F, psi	1700	D650–41T
Stiffness, 77°F..................	13,300 (1)	D747–43T
Impact, Izod, 70, 77, 170°F ft-lb/in.	(3)	D256–41T
Rockwell......................	13R	ARL. M–29
Flow temperature, °C............	104	D569–43
Deformation under load, 122°F, %. .	20 (4)	D621–43
Strain release temperature, °C.....	75–80	ARL. M–15
Yield temperature, °F............	140 (1)	ARL. M–8
Heat distortion temperature, low load, °F....................	122 (5)	D648–42T
Specific heat, cal/gm/°C..........	0.5	
Coefficient of expansion per °F....	10.5×10^{-5}	D696–42T
Thermal conductivity, Btu/hr ft^2/°F/in....................	2.96	D325–31T
Dielectric strength, step by step, v/mil	1000 (6)	
Volume resistivity, ohm-cm	10^{17} (6)	
Power factor, 60, 10^6, 10^8 cycles....	Less than 0.0005	
Water absorption, %............	0.01	D570–42
Flammability, in./min............	Ignites and burns slowly	
Outdoor exposure................	No discoloration (7)	
Accelerated weathering...........	No discoloration (7)	
Methods of working.............	Inj., compr., extr., cal.	
Basic color....................	White translucent (8)	
Resistant to....................	Water, alkalies, acids, and oxygenated solvents	
Not resistant to................	Chlorinated solvents, aliphatic and aromatic hydrocarbons at elevated temperatures	
Outstanding for.................	Moisture resist., elect. prop., toughness, workability	
Major uses....................	Electrical insulation, tubes, containers	

NOTES

(1) Average values reported. May vary considerably with method of specimen preparation (inj., comp., ext., etc.).
(2) Tensile tests made of speed of 1 in./min.
(3) Does not break at room temperature in 4 ft-lb machine. 0.50 ft-lb at −70°F.
(4) Tests run at a load of 1200 psi since the 4000 psi loading of the standard test was designed for more rigid plastics.
(5) Maximum fiber stress 66 psi.
(6) Values given are for early experimental polythene.
(7) Tensile strength and elongation drop in absence of stabilizer.
(8) For electrical purposes, antioxidant is added which gives a light brown color.

Source: E. I. du Pont de Nemours & Company, Inc.

had gone into items for the armed services. The new material had demonstrated its advantages as a covering for electric wiring and cable, particularly for high frequencies.

The following table gives properties of Carbide and Carbon Chemicals Corporation's electrical grade of polyethylene:

Specific gravity	0.92
Specific heat (18°–40°C)	0.53
Softening temperature, °C (transparency point)	105
Water absorption, % weight gain, 100 hr at 25°C	0.03
Linear coefficient of expansion, cm/cm/°C	25×10^{-5} (above 115°C) Varies below 115°C
Tensile strength, psi	1800
Elongation, %	600
Impact strength, ft-lb $in.^{-1}$ notch	3
Brittleness temperature, °C	Below minus 70°C
Dielectric constant, 50 mc	2.29
Power factor $\times 10^{-5}$	30
Volume resistivity, megohms-cm	10^9

NYLON AS A PLASTIC

Nylon conforms to the common definition of a plastic — a material that can be formed to a desired shape under heat and pressure, but its use as a plastic was delayed until the war by the tremendous demand for it for hosiery and brushes and the lack of time for complete research and development. An injection-molding composition of nylon that possesses extreme toughness and high softening temperature has now been produced for military uses. E. I. du Pont de Nemours & Company, Inc., has announced that nylon plastic will be available to industry after the war. Nylon molding powder has been designated as FM-1 and has the properties shown in the accompanying table.

Properties. Nylon is a thermoplastic and has the highest service temperature and the greatest toughness of any plastic of equal rigidity. Most thermoplastics soften in the neighborhood of 160°F. The highest softening point previously attained was about 280°F. Nylon plastic, under no load softens at around 450°F., and molded

articles retain their form stability to 350°F. The softening point is about equal to the charring point of some of the thermosetting materials. Nylon plastics having even higher softening points may be formulated.

For thin molded sections that have great strength, nylon will do a job impossible for many other materials. One observer stated, "One military nylon molding, for example, looks something like a tiny wooden matchbox, except that the sections are thinner and it appears more fragile. But you can step on it — and though it gives somewhat, it comes right back to its former shape."

Nylon has other advantages. It is one of the lightest plastics, having a specific gravity of 1.14 compared with from 1.27 to 1.56 for cellulose acetate.

Nylon involves no fire hazard since it has an extremely slow burning rate. Time has little effect on it; it does not rot or deteriorate with age. Sunlight has slight effect. Nylon is inert to metal inserts. Its chemical resistance compares favorably with that of other thermoplastics, and it is not attacked by oil, grease, most solvents, alkalies and weak acids. It is easily machined and can be molded in existing presses with a few minor modifications.

In general, nylon is advantageous for molded pieces because of mechanical properties rather than appearance. The molding powder is produced commercially in black and translucent light cream colors. The lack of effective solvents makes the incorporation of dyes a difficult problem and also complicates the development of a satisfactory cementing technique. However, experiments now being conducted indicate that the color range may eventually be extended to include most translucent and opaque colors.

Nylon molding powder requires a high injection temperature, melts sharply to fluid condition, and sets quickly. The best injection molding results have been obtained with a screen pack which provides not only a shutoff but a screen for the removal of unmelted particles.

Dies designed for conventional thermoplastics generally require modification because FM-1 nylon has a high mold shrinkage of 0.012 in. per in. Because the material is molten when it enters the

die, knockout pins should fit closely and mating surfaces should be ground for perfect contact.

APPLICATIONS. The first strictly plastics application of nylon was for bearings. A few were made before the war, were installed for testing at du Pont rayon plants, and are still under study. They require no lubricant for a light load at high speed or a heavy load at low speed. Water is the only lubricant needed under any condition. They may be industrially important after the war.

Courtesy E. I. du Pont de Nemours & Co., Inc.

FIG. 6. Molded nylon is gradually finding its place in industry. Here is one of the recent applications.

Several small parts of important military equipment have been made from nylon molding powder. It is reported that their performances have been uniformly good. Two or three molders report that articles made from nylon are outstanding in their toughness and resistance to heat and abrasion.

One military application of nylon plastic is tubing. Extruded much like macaroni, the thin-walled tubes are tough, flexible and resistant to oils, chemicals and heat.

Nylon films are characterized not only by their toughness, but by their resistance to chemicals and moisture. They have had ordnance applications. In the laboratory, nylon film has been pro-

nounced good for a vacuum package, where strength, airtightness and abrasion resistance are required.

Nylon in solution, which forms a film when applied, has been used to insulate electrical wires. The wire is coated by running it through a solution at the rate of a mile a minute. In addition to good electrical properties, resilience and absence of fatigue adapt nylon to this use. Nylon in solution has also been used to coat fabrics and has numerous other possibilities.

Among the many nylon plastic articles either suggested for the future or in limited use now are the following:

Strips of nylon for outdoor furniture. According to tests, they do not deteriorate with age, are elastic and weather-resistant, and outwear and outlast natural rattan. Smooth and easy to clean, nylon strips may be used to cane bus, subway and trolley car seats.

Fabrics coated with nylon. They are shiny but wear well and do not crack or scuff. They can be made to resemble kid or calf and are suggested for shoes, handbags and luggage.

Carburetor diaphragms of nylon fabric coated with either nylon or neoprene, which resist deterioration from oil or gasoline.

Zippers. They have been molded of nylon experimentally and illustrate well the material's great strength in thin sections.

OTHER NEW NYLON APPLICATIONS. Cords for bomber tires and window screening are among the newest and most interesting applications of nylon. Window screens of nylon can be produced in any color, will not stain the surrounding woodwork, will not corrode, and require no painting. Tests indicate that they have unusual durability. Nylon screens will not have to be taken down in the fall and put up in the spring. They can be rolled up and down on tracks like a window shade.

Tire cords of nylon are the strongest yet made. Developed since the war began, they have already proved satisfactory on bombers. A 25-ton airplane lands at a speed of 100 miles an hour or more on small front-line fields. When the brakes jam on, the tread portion of a tire carcass actually buckles and folds back on itself. Nylon withstands this. Tires with nylon cords require less rubber than other types.

TYPICAL PROPERTIES OF FM-1 NYLON

Property	Test Result	Test Method
Specific gravity	1.14	ASTM D71-27
Tensile strength, 70, 77, 170°F, psi	16,620 (1); 10,530; 9,290 (2)	ASTM D638-42T
Elongation, 70, 77, 170°F, %	3% (1); 54%; 145% (2)	ASTM D638-42T
Modulus of elasticity, 77°F, psi	325,500	ASTM D638-42T
Flexural strength, 77°F, psi	12,600-14,600	ASTM D650-42T
Stiffness, 77°F	1.89-2.02 (3)	Arlington M-9
Impact, Izod, 70, 77, 170°F ft-lb/in.	0.418; 0.944; 0.968	(8) D256-41T
Rockwell	100 L65 H	Arlington M-29
Creep in flexure	89 (4)	Arlington P-25
Deformation under load, 122°F, %	4.0	ASTM D621-41T
Heat distortion temperature, °F	149	ASTM D648-41T
Heat distortion temperature-low load, °F	403 (5)	ASTM D648-41T
Specific heat, cal/gm/°C	0.55	
Coefficient of expansion per °F	5.7×10^{-5}	ASTM D696-42T
Thermal conductivity, Btu/hr/ft^2/°F/in.	1.74	ASTM D325-31T
Dielectric strength, short time, v/mil	400	ASTM D149-39T
Dielectric strength, step by step, v/mil	300	ASTM D149-39T
Volume resistivity, ohm-cm	10^{13}	ASTM D257-38
Dielectric constant, 60, 10^6 cycles	3.8 (6); 4 (7)	ASTM D150-41T
Power factor, 60, 10^6 cycles	1.8 (6); 5 (7)	ASTM D150-41T
Water absorption, %	1.5	ASTM D570-42
Flammability, in./min	Self-extinguishing	ASTM D635-41T
Methods of working	Injection, compression, extrusion	
Basic color	Light cream	
Resistant to	Esters, ketones, alkalies, alcohols, common solvents, weak acids	
Not resistant to	Phenol, formic acid, conc. mineral acids	
Outstanding for	Toughness, high temp. resistance	
Major uses	Heat-resistant parts	

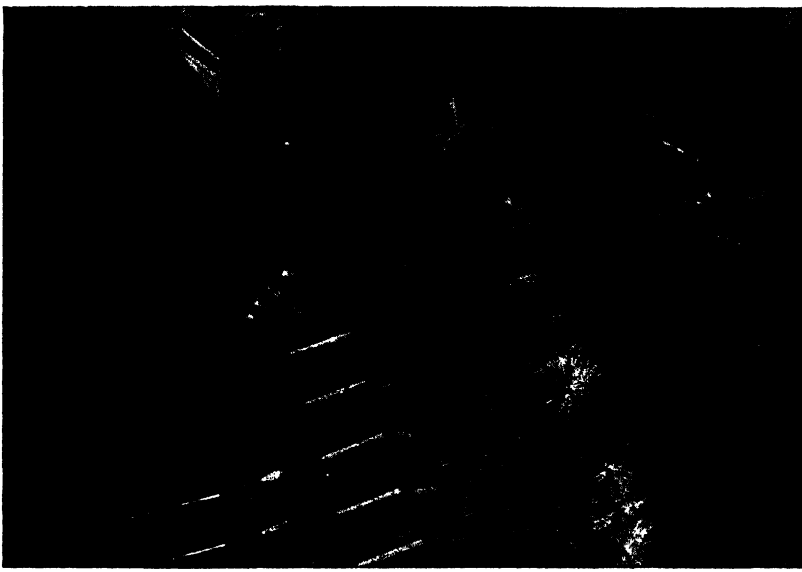
NOTES

(The Numbers in Parentheses in the Data Refer Specifically to Deviations from Accepted Test Methods)

(1) −58°F
(2) 140°F
(3) Millimeters deflection at 0.125 in. thickness
(4) Mils after 48 hr of 1600 psi and 77°F minus original deflection
(5) 64 psi — D 648-41T mod.
(6) 33°C dry
(7) 22°C, 18% RH, 10 cycles
(8) Type R conditioning

Another possible postwar market for nylon is drapery and upholstery fabrics. A lace curtain of nylon may relieve housewives of the tedious task of drying curtains on stretcher frames. Inherent crush resistance gives nylon a distinct advantage in pile fabrics, such as velvet, plush, mohair and frieze. Nylon fiber may also find new uses for shower curtains, rainwear, slip covers and a wide variety of garments.

One of thc most important wartime developments of nylon has been tapered form for paint brushes. Said to be the first satisfactory



Courtesy E. I. du Pont de Nemours & Co., Inc.

FIG. 7. The use of plastics for industrial brushes has contributed much to industry.

synthetic paint brush ever made and to wear at least three times longer than pig bristle, the tapered form was achieved by pulling a continuous nylon filament from a spinneret at a controlled variable speed. Such bristles have been found to possess the required strength, resilience and inertness to ingredients for paint brush use. Before the war nylon was used in 90 per cent of the better quality tooth brushes in the country and 50 per cent of the hair brushes. It is

predicted that after the war virtually all tooth brushes and hair brushes, except the very cheapest, will have nylon bristles.

More than 20 different types of industrial brushes, ranging from textile printing and bottle washing to sewerage cleaning and electroplating, were bristled with nylon when the material was available. Many new industrial and household brushes will be made when nylon again becomes available after the war.

SUMMARY. Nylon is certainly one of the most promising new materials that have thus far been developed, and its use in the postwar years will grow enormously. At the time of Pearl Harbor productive capacity for making nylon was about 8,000,000 lb. annually, and it has been expanded greatly since then to meet military demands, the most important of which was for making parachutes.

Some idea of the vast size of the market available to nylon after the war is suggested by the fact that, if it completely displaces silk, as many predict, that alone would require about 50,000,000 lb. a year. If it displaces pig bristle and brushes, a further 5,000,000 lb. annually might be required, and this does not take into consideration the amount of nylon that might be used in place of rayon, cotton, wool and other fibers, or its many other uses. According to the du Pont Company, only about 11 distinct types of nylon have been developed, while the number theoretically possible runs into the thousands.

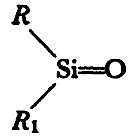
THE SILICONES

A new family of commercially available plastics, known as the silicones or silanes, has recently resulted from extensive research work on the part of several leading resin manufacturers, notably Dow Corning Corp. and the General Electric Co.

One of the drab and uninteresting facts learned by the student of high school chemistry is the relationship of carbon and silicon in the periodic table of the elements. This apparently unimportant fact has been utilized practically in the development of the silicones.

Early patents issued to Eugene G. Rochow, and assigned to the General Electric Co., indicate the chemistry involved in synthesizing this new group of plastics.

Silicones are of the general chemical type indicated by polymers of the following chemical formula:



In this formula, R and R_1 consist of various organic groups on radicals including both aliphatic and aromatic members. For example, R may be a methyl (CH_3) group and R_1 may be a phenyl (C_6H_5) group.

The replacement of carbon by silicon, to form silicones, was known at an early date as indicated the formation of ethyl, propyl and other silicones mentioned in the *Journal of the Chemical Society* 95, 302, under the authorship of Kipping and Martin; and in subsequent volumes 101, 107 and 123 of the same publication.

In what is believed to be its first commercial application, the commonly known Grignard reaction is used in preparing silicones from silicon tetrachloride, the silicon bearing chemical.

Methyl magnesium bromide is reacted with silicon tetrachloride ($SiCl_4$) to produce the mono- and di-methyl silicon chlorides.

$$CH_3MgBr + SiCl_4 \rightarrow CH_3SiCl_3 + MgBrCl$$

$$CH_3MgBr + CH_3SiCl_3 \rightarrow (CH_3)_2SiCl_2 + MgBrCl$$

These silicon derivatives remain in ether solution and may be separated from the magnesium salts, although this step is not necessary.

A characteristic method of preparation follows:

An ether solution of 1.75 mols of methyl magnesium bromide is added slowly and with rapid stirring to an ether solution containing 1 mol of silicon tetrachloride, the latter being cooled to minus 68°F., or lower, prior to the addition of the former. The reaction rate must be controlled so that at no time does the temperature rise above 32°F.

Following this reaction, the methyl silicon chlorides are hydro-

lyzed by pouring the mixture over cracked ice.

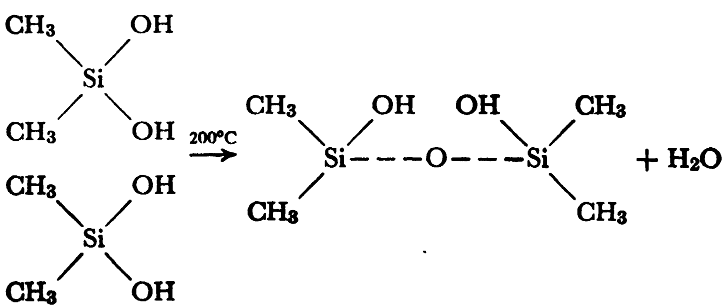
$$CH_3SiCl_3 + 3H_2O \rightarrow CH_3Si(OH)_3 + 3HCl$$

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

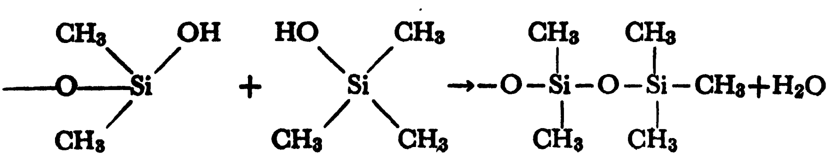
These hydroxy compounds readily condense with loss of water to form initial and intermediate condensation products. Those products are soluble in ether and may be removed from the ether layer by usual chemical fractionating means. Free acid is removed from the ether solution by frequent washing with water, and the ether solution is then evaporated until a viscous liquid mass is obtained.

By subsequent heating at 392°F. for a requisite period of time clear, colorless, hard resins are obtained.

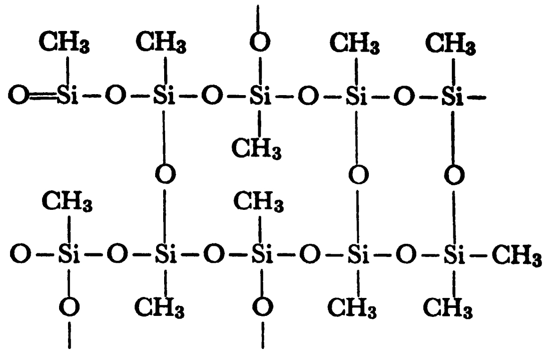
This resin polymer is believed to be essentially a network of silicon-oxygen chains in which the methyl groups are linked to the silicon atoms. Thus, when dimethyl silicol condenses, the reaction probably proceeds thus:



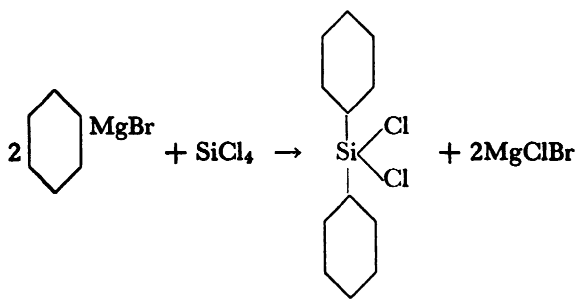
Such chains of alternate Si and O atoms may be terminated by an OH group, which may react further, or by an $-Si(CH_3)_3$ group which is unable to react further:



Eventually this cross linkage may be expressed as follows:



When phenyl magnesium bromide is reacted with silicon tetrachloride, phenyl silicones result.



Silicone resins find commercial application in the field of electrical insulation. They may be used in varnish form to coat wire, or as paper impregnated sheets for insulation, or in conjunction with fillers as molded insulation. They are characterized by excellent electrical properties, low moisture absorption, high heat resistance and durability.

Insulation Coating Composition. Bare copper wire, or covered wire, is covered with a solution of silicone in a volatile solvent. The latter is removed by baking, which at the same time polymerizes the silicone to a polymeric insoluble form.

Sheet Insulation. Paper, organic or inorganic fabrics or felts

are impregnated with silicone in solution. Subsequent baking removes the solvent and polymerizes the silicone.

PROTECTIVE COATINGS. Silicones may be used for protective coating of glass bulbs, or other articles which may be exposed to abnormal heat conditions or hot flying particles. Items so coated are rendered practically shatterproof.

CONDUCTIVE POINTS. By including varying amounts of conducting materials such as graphite in the silicone resin, paints may be obtained having any desired degree of electrical conduction.

SEALING COMPOSITION. Silicone resins may be used for sealing metal to glass. Such joints may be made vacuum-tight. Applications of this sort are used in the manufacture of radio tubes.

Silicones are compatible with a variety of gums, resins and plastics, these including phenol-formaldehyde resins, urea-formaldehyde resins, vinyl resins, cellulose esters, shellac and many others.

Many other uses of silicone resins are known, but owing to wartime restrictions, they may not be developed at this time.

Two companies that have done much work in developing the silicones are Dow Corning Corp. and General Electric Company. While their use has been closely connected with the war effort, it is quite reasonable to expect that they will find important peacetime applications in view of their high resistance to heat and their good electrical properties. Dow Corning Corp. in cooperation with Dow Chemical Company has developed silicon based materials having resistance to elevated temperatures to be used as a bonding material with glass fibers.

The silicones range through viscous fluids to resins for varying types of applications. All have one property in common, the ability to withstand high temperatures, which is characteristic of their silicon parentage. In addition to high temperature resistance the new fluids are characterized by ability to remain pourable liquids at temperatures far below zero.

The silicones also exhibit rubber-like properties with respect to elasticity and rebound.

One established silicone resin, known as 990A (Dow) has the following properties:

Type	Organo silicone
Color	Brown
Viscosity	Variable from 0.5 poise upward to 1.5 poise
Solvent	Toluol used at present but methylethyl ketone can be substituted
Dielectric strength	1400 to 2200 v/mil (Standard ASTM ¼ in. electrode short time test on 4 mil cloth built up to 10 mils over all. This value increases with continued heat-treatment. Sample cured to tackfree conditions had a dielectric strength of 1400 v/mil and after 100 days at 350°F (177°C) its value was increased to 2200 v/mil.)
Power factor at 60 cycles	(Taken at room conditions on a Schering bridge after conditioning 2 hr at 225 F) 0.35 to 0.5 *Note:* Tests conducted by an outside laboratory revealed that power factor at 1000 cycles was approximately the same.
Film buildup	A 50% solid solution will build up to approximately 0.0015 in. per side of 4 mil cloth per dip.
Insulation resistance	Taken at 90% RH, 100°F, 225 volts dc Specimen size — 1 in. × 1 in. × 0.010 in. — 1500 megohms
Oil resistance	Will pass ASTM test method
Effect of heat aging at 350°F (177°C)	After 18 months in an enclosed oven equipped with circulating fan, the following was observed:

1. Discoloration. Only slight darkening. Standard materials have turned black.
2. Film thickness. No loss.
3. Flexibility. After 18 months, sheet could still be bent around 3/16 in. mandrel without film cracking. (Thickness of test specimen was 0.010 in.)
4. Dielectric strength. (Short time ASTM — ¼ in. mandrel). Gradually increased from 1600 v/mil to 2750 v/mil and remained constant.

Recommended Procedures in Handling. 1. *Magnet Wire.* Standard wire machines can be used by making proper temperature and speed adjustments. Depending upon the exact type of wire prepared by the specific manufacturer, these two variables can be altered over a wide range. Wires have been produced at speeds from one-half that normally used up to 6 ft. per min. faster than standard. In all cases, temperature was higher, ranging from 104°F. (40°C.) to 212°F. (100°C.) above normal. Test data indicate that a wire having very good appearance and exhibiting

satisfactory properties otherwise was manufactured at 700°F. (370°C.), 4 dips, at a speed of 17.4 ft. per min. in a 16 ft. horizontal oven.

On double Fiberglas wire, impregnation can be accomplished by passing through the solution after both serves have been applied. If more satisfactory adhesion and better abrasion properties are desired, it is recommended that a pass through the resin between the two serves be given. This latter procedure will, however, increase over-all buildup by a slight amount.

2. *Motor Assemblies, Transformer, and Solenoid and Magnet Coils.* Wound coils should be preheated at 275°F. (135°C.) for 2 hr. and then immediately submerged in the resin which should be approximately at room temperature. After remaining in the resin for ½ hr., they should be removed, allowed to drain and air dry for 2 hr., and baked for 6 hr. at 480°F. (249°C.) in an oven equipped with a fresh air intake and exhaust. Additional dips do not require preheating nor should they be dipped immediately upon removal from the oven. Two coats will usually produce a satisfactory job; however, more can be applied depending on the requirements of the object being impregnated.

3. *Varnished Fiberglas Cloth.* Large sheets of varnished Fiberglas have been made in the laboratory by hand dipping and curing at 500°F. (260°C.) for 5 hr. each dip. Varnish tower application has not so far been attempted, but experimental tapes have been made on a wire impregnating machine. The temperature used was 700°F. (370°C.) for about a 1-min. pass through the oven.

The tape thus produced was somewhat brittle, indicating that lower temperatures can be used. Continued work on this product is required and planned.

POLYVINYL CARBAZOLE (POLECTRON)

This is a new material that was developed first in Germany some time before the war. General Aniline & Film Corporation holds American patents and started working with the material early in 1941. It has sometimes been referred to as "synthetic mica," but such a designation is not accurate, for Polectron, though it possesses

some of the properties of mica, cannot be considered a satisfactory substitute in all its applications.

Polectron polymer is polyvinyl carbazole, a new thermoplastic resin. It is technically important, according to its maker, because of excellent electrical properties that are particularly suited to applications in the electronics field. The polymer combines low power factor, high heat distortion temperature, high dielectric strength and good chemical stability. When properly compounded it can be injection and compression molded. A special technique has been developed for impregnation of electrical equipment without use of solvents.

In the preparation of Polectron polymer, acetylene and carbazole are combined chemically to form monomeric vinyl carbazole. Polyvinyl carbazole is then prepared by polymerization under special conditions.

Polectron polymer is resistant to water, dilute acids, alkalies and hydrogen fluoride but is attacked by concentrated sulfuric and nitric acids. It is swelled or dissolved by most aromatic and chlorinated hydrocarbons, esters and ketones but is insoluble in aliphatic and hydroaromatic hydrocarbons, alcohols, ether, carbon tetrachloride and paraffinic mineral oils. Good solvents are benzene, toluene, xylene, chlorbenzene, ethylene dichloride and trichlorethylene. Polectron polymer is unaffected by oxygen except at relatively high temperatures. Sunlight causes slight discoloration.

Polectron polymer has important applications as a dielectric material for electrical condensers. Its properties permit relatively high temperature and high voltage operation.

Polectron polymer compositions can be compression molded in the range of 356° to 464°F. and injection molded between 446° and 626°F. Lower molding temperatures can be obtained, but the characteristic high heat distortion temperatures will also be lowered. The limitations of molded Polectron polymer are low flexural and impact strengths. However, it appears suitable for uses where mechanical properties are distinctly secondary to electrical properties and heat distortion temperature. It is being considered for specialty items in coil forms, cable connector parts, switch parts, coaxial cable spacers, stand-off insulators, etc.

PROPERTIES OF POLECTRON POLYMER

Dielectric constant, 25°C, 1 kc to 100 mc	3.0
Power factor, 25°C	
1 kc to 100 mc	0.0004–0.001
After 48-hr water immersion, 1 mc	0.0025–0.004
Dielectric strength, v/mil	
For 0.1 in. thickness	750–1000
For 0.001 in. thickness	3000
Volume resistivity, ohm-cm	10^{14}–10^{15}
Surface resistivity, 25°C, 50% relative humidity	10^{14}–10^{16}
Linear coefficient of expansion per °C × 10^6	45–75
Heat distortion temperature, ASTM	100–150°C*
Specific heat, cal/gr/°C	0.3
Flexural strength (−20° to 80°C), lb/in.^{2}	4500–5500†
Impact strength, ft-lb/in. of notch	0.5–1.0†
Specific gravity	1.2
Molding temperature	
Compression	180–240°C*
Injection	230–330°C*

* Depending on plasticizer content.
† Special compression-molded composition.

STYRAMIC POLYDICHLOROSTYRENE

This new polymer has been developed by Monsanto Chemical Company as a material of high heat resistance retaining in full (or bettering) the electrical insulating characteristics of polystyrene. A heat distortion point (A.S.T.M.) of 236°F. is its most important physical characteristic. Another important property is dimensional stability secured in part by a water absorption value of 0.03, half that of polystyrene.

In addition to good heat resistance the styramic polymer (designated as styramic HT polydichlorostyrene) has electrical characteristics somewhat better than polystyrene, enabling its use in ultra-high-frequency work. The curve of power factor remains virtually flat throughout the frequency range. Data on most applications are restricted and cannot be published at present.

The high heat resistance does not mean unduly high molding temperatures. The molding range of this material is 475° to 550°F., still within the range of standard injection or extrusion machines. The material has excellent color possibilities, being basically a

clear transparent, although its applications are not likely to be those where color or appearance is of prime importance.

It is nonflammable; is self-extinguishing when subjected to the A.S.T.M. flammability tests and is nearly 25 per cent heavier than polystyrene.

Production of the new compound is on a pilot-plant scale and available only in small quantities for direct military applications.

Cost is fairly high thus limiting its field to specialized uses.

PENACOLITE

Pennsylvania Coal Products Co., the principal producer in this country for the past 20 years of the organic chemical resorcinol, has recently developed a large series of resorcinol-formaldehyde resins. These resins are two-stage, phenolic type requiring the addition of approximately 10 per cent setting agent to convert them to their final thermosetting form. Although phenolic in character they possess many properties not commonly associated with the conventional phenolic, the most outstanding undoubtedly being their low temperature of cure. Because of the increased polarity of the resorcin molecule over the phenol molecule, the resulting resins are not similar with respect to such characteristics as solubility, compatibility and adhesion.

Through utilization of this property of low temperature of cure, several room-temperature setting, phenolic type, neutral, wood-to-wood adhesives are now being produced. These adhesives have shown very high strength and produce a bond which is weatherproof to the highest degree. The Forest Products Laboratory at Madison, Wisconsin, has thoroughly tested these adhesives and has reported favorably on their properties. Many difficult wartime bonding problems involving wood or similar materials are now being successfully solved by the use of these adhesives.

Although designed principally for the bonding of wood, they have been found equally satisfactory for bonding laminated phenolic plastics material. Another unusual characteristic is that for some unaccountable reason the resorcinol resins and adhesives adhere tenaciously to nylon in both the sheet and the fiber form.

Several manufacturers of metal-to-metal adhesives, which in themselves have to be cured at elevated temperatures, have expressed interest in using room-temperature setting Penacolite-adhesives in conjunction with their metal primer to bring about the bonding not only of metal to metal but of metal to plastic and metal to wood at low temperatures.

NEW ALKYD RESINS

A new class of alkyd resins recently developed by American Cyanamid Company is reported to have greater hardness, higher melting point, an increased rate of cure and much faster drying time than the older alkyd resins.

Alkyd resins are usually formed by the reaction of polyhydric alcohols with polycarboxylic acids with or without modifying substances. Although trihydric glycerol is the polyhydric alcohol ordinarily employed in the manufacture of alkyd resins, dihydric, tetrahydric and hexahydric alcohols have also been used to give resins of particular characteristics. Glycol pentaerythritol and sorbitol may be mentioned as examples of each.

The new class of alkyd resins is prepared by replacing at least a substantial portion of the polyhydric alcohol with dipentaerythritol.

Dipentaerythritol is a hexahydric ether alcohol of the formula $(CH_2OH)_3C.CH_2OCH_2.C(CH_2OH)_3$ and is unique in that it contains six primary alcohol groups. Many of the unusual properties of the new alkyd resins are due to these six primary alcohol groups. Dipentaerythritol is a white powder having a melting point of 430°F., a hydroxyl value of 1310 and a very low solubility in water and organic solvents. Most esters of this alcohol with mono- and polycarboxylic acids share the water resistance of the alcohol so that the resins prepared therefrom, including those modified with drying oil fatty acids, are characterized by excellent water resistance.

The unmodified alkyd resins prepared from dipentaerythritol with most dibasic acids are brittle materials with high melting points. The rosin-modified product is also a hard brittle material.

Monohydric alcohols, such as ethyl, butyl, benzyl, cyclohexyl, and lower polyhydric alcohols, such as glycol and glycerol, when added to the reaction mixture tend to soften the product, lower its melting point and increase its solubility in organic solvents. Saturated aliphatic acids, such as acetic, butyric, palmitic, stearic, also have a softening effect on the resin and increase its solubility.

Although the straight alkyds described above are useful for many purposes such as impregnating paper in the manufacture of imitation parchment, in finishing textiles and as a binding agent in abrasive blocks, the new alkyd resins are probably of greatest value in the preparation of fatty-acid-modified alkyd resins, and particularly those which are oxygen-convertible. These products are prepared by reacting dipentaerythritol, a polycarboxylic acid and an unsaturated monocarboxylic acid or an oil which on hydrolysis yields unsaturated fatty acids.

The new resins may be used for many purposes analogous to those for which ordinary alkyd resins have been employed. The modified alkyd resins should be particularly useful because of their rapid air-drying properties and improved water resistance in the preparation of printing inks, including painting pastes to be applied to cloth, in the manufacture of linoleum, also in the preparation of rapid-drying enamels, paints, varnishes and the like. They are compatible with cellulose nitrate, cellulosic ethers such as ethyl cellulose, urea resins and melamine resins, cyclized rubber derivatives, and many other materials.

Bakelite's XRS-16631

Bakelite Corporation also has developed a new vinyl alkyd resin known as XRS-16631, which has received considerable attention in connection with war work. Very little information is available on this new material, however.

Aroplaz

Another new alkyd resin, known as Aroplaz 1244, has been developed by Stroock & Wittenberg, Division of U. S. Industrial Chemicals, Inc., to meet the requirements of a new Maritime Com-

mission specification, calling for a long, pure-linseed-oil modified alkyd resin.

Aroplaz 1244 has been thoroughly tested in the formulation of paints based on the following two new U.S.M.C. primer specifications:

52–MC–23 primer red lead, quick-drying (synthetic). This specification supersedes MC–52–A–1 (Class XXII)
52–MC–29 primer, zinc chromate.

The new resin is said to possess the following physical constants:

Viscosity (G-H) at 70% solids	Y minus-Z1
Viscosity (G-H) (when thinned further to 50% solids in mineral spirits)	C-G
Color (G-H 1933)	7–12
Acid value of plastic	Below 10
Wt/gal at 25°C at 70% solids	7.92–8.08 lb

Still another development, interesting not only from the viewpoint of performance, but particularly because of its availability, is Stroock & Wittenberg's Aroplaz 1306 Solution (75 per cent solids in mineral spirits). The physical constants of this new resin are:

Viscosity (G-H) at 75% solids	Y-Z1
Color (G-H 1933)	7–9
Acid value of plastic	10–20
Wt/gal at 25°C at 75% solids	7.9 lb

The solution is so adjusted that, when reduced to 50 per cent solids, the viscosity is suitable for use as a normal enamel vehicle.

Excellent white enamels can be produced with this material, approaching the whiteness obtained with the usual alkyd types.

Aroplaz 1306 has good color retention when compared with maleic resin varnishes, and is far superior to ester gum and phenolic resin varnishes.

TETRAFLUORETHYLENE POLYMER

A new plastics material, tetrafluorethylene polymer, has been developed by E. I. du Pont de Nemours & Company, Inc. Use of this material has been confined to war work, and very little information regarding it is as yet available, although it is anticipated that it will have postwar applications.

Material is formed by the polymerization of tetrafluorethylene. The polymers are white or brown powders or jellies which are insoluble in the usual solvents and are inert to the usual chemical reagents. These polymers become incandescent in the presence of a flame but do not burn when the flame is removed, and melt only at red heat. The polymers are insoluble in hot or cold water, acetone, ether, petroleum ether, ethyl alcohol, iso-amyl alcohol, carbon tetrachloride, $C_2F_3Cl_3$, dichlorobenzene, ethyl acetate, pyridine, nitrobenzene, 30 per cent NaOH, petroleum oil, glacial acetic acid, concentrated sulfuric acid and concentrated nitric acid.

By the use of highly specialized molding techniques, the polymers can be made into articles which are light colored and in thin sections relatively clear. Molded articles have a tensile strength at 77°F. of 1500 to 4000 lb. per sq. in., depending on the method of fabrication, and on elongation of 200 to 500 per cent. Cold toughness is good and the polymer can be flexed at −94°F. without breaking. The density varies from 2.1 to 2.2. The polymer has a solid phase transition temperature of 620°F., above which there is disorientation, loss of crystalline structure and a drop in strength.

The exact physical properties of tetrafluorethylene are not yet known. It is anticipated that the impact strength (Izod) will be of the order of 3 to 4 ft.-lb. per in. of notch. The extreme fiber strength (flexural) should be in the neighborhood of 1000 lb. per sq. in.

The inertness of this polymer to chemical reagents, its insolubility, and its resistance to heat and to fire make its use desirable in many places. Expected applications are laboratory apparatus for handling corrosive reagents, and disks for goggles used in corrosive atmospheres, such as those which pervade certain chemical plants. The material may also be extruded into fibers which may be used in the manufacture of heat-resistant clothing and the like.

FOSTERITE

This is a new solventless impregnant giving 100 per cent fill. Developed by Westinghouse Electric and Manufacturing Company it has been used during the war in electric and radio com-

munication equipment for the armed forces, but it is anticipated that it will have wide commercial uses after the war.

It is evident that solvent type varnishes which are 50 per cent solvent cannot give more than 50 per cent fill. The two most desirable but elusive properties of such materials are (1) usability without a solvent, (2) a 100 per cent filling of all space within the insulation. It is claimed that these properties have been obtained in Fosterite. During the impregnation of the coil or device, Fosterite is in a liquid state, but the "solvent" reacts with another resin dissolved in it and the whole mass turns to a tough solid. It is solventless in that the whole of the liquid resin reacts under heat to form the infusible solid: there are no by-products of the reaction that must escape as in most resin reactions.

The additional problem of keeping the resin from running out while it is being polymerized to a solid has been solved, resulting in both a satisfactory material and a satisfactory processing method. Actually, this is not one resin, but a family offering a wide range of properties through suitable modifications.

The complete filling allows much higher voltage gradients to be used than for normal materials. On one small radio transformer, for example, Fosterite provides four to five times the dielectric strength that was obtained with former materials. This permits a radical reduction in size and weight.

Moreover, the elimination of voids in coils increases the heat conductivity of the structure. Preliminary experiments have shown that certain coils impregnated with Fosterite resin will dissipate as much as one-fourth more heat than coils impregnated with ordinary solvent-type varnishes. In addition, a sample of Fosterite, heated in transformer oil at a temperature of 185°F. (85°C.) to 194°F. (90°C.) for one year, swelled less than 1½ per cent — indicating that it is insoluble in transformer oil and hence suitable for treating oil-insulated coils.

While Fosterite was developed as a solventless varnish for use in standard electrical equipment, it is also finding application in highly specialized communication equipment for the armed services where moisture-proofing is the most critical factor.

Surface coating has also provided a radical improvement in

moisture resistance of such apparatus. By means of the coating and impregnation, the moisture-proofness is said to be 100 to 1000 times better than by the use of the best previous materials.

THE USE OF SULFUR IN PLASTICS

Sulfur is one of the basic chemical elements and it is also one of the cheapest of all materials. For years the price has been $16.00 per long ton at the mine and $17.50 f.o.b. at Gulf ports. This works out to about $0.008 per lb., which is obviously much cheaper than a great majority of other materials now used in the plastics industry. It is therefore not surprising that sulfur should be the object of considerable research in the field of plastics.

The following is a brief summary of some of the developments now under investigation:

Perhaps the most promising development has been the reaction of the olefin resins with sulfur dioxide. These resins are thermoplastic, transparent and water-white. They are easily molded and have good resistance to chemicals. In addition to several excellent properties, they are potentially cheap, perhaps as low as $0.025 per lb.

Chief disadvantage is that they have not been stable and continue to liberate sulfur dioxide. Considerable research is now under way on the olefin resins, particularly by Phillips Petroleum Company, which has furnished the following summary:

Phillips has developed a strong patent position in this field, particularly in connection with the production of resinous compounds by the reaction of various unsaturated organic compounds with sulfur dioxide. The possibility of producing plastics from the enormous quantities of inexpensive raw materials made this reaction of especial interest. Much pilot-plant and semicommercial scale work has been done on a process leading to the commercial production of olefin-sulfur dioxide resins. In addition to the patents which have already been issued to Phillips many applications still are pending.

The resins can be produced by reacting in the liquid state a wide variety of mono-olefins or mixtures of olefins, with sulfur

dioxide, in the presence of suitable catalysts. The heteropolymeric products obtained are thermoplastic, permitting the production of coherent moldings, in some instances colorless and transparent. The properties of the resins produced from the 1-olefins vary in steady steps as the molecular weight of the olefin increases from that of ethylene, which produces an insoluble resin possessing a high softening temperature to that of 1-decene resin, for example, which is soft and rubbery at ordinary temperatures, and is soluble in many common organic solvents. The resins from 2-olefins have higher softening points, are generally less soluble, and are more resistant to alkalies than those of the isomeric 1-olefins.

The reaction may be catalyzed by a variety of materials, including peroxides and certain nitrates. Light of less than 3000 Angstroms wave length also serves to promote the polymerization. This polymerization reaction exhibits an unusual temperature effect, in that the reaction will not occur above certain temperatures, which differ for different olefins.

Although the resins decompose when heated well above the softening points, there are fairly wide ranges of temperature within which they can be satisfactorily molded under pressure. Propylene resin can be molded in the range of 180° to 200°C. (356° to 392°F.), and *n*-butene resins in the range of 125° to 180°C. (257° to 356°F.). Plasticizers, fillers and pigments may be incorporated in the resin to produce desired modifications. Asbestos fiber and wood flour fillers are satisfactory and produce molded articles which are tougher than the original resin with only a slight decrease in the tensile strength. Plasticizers can be used to increase the ease of molding and decrease brittleness of the resins.

These resins are resistant to dilute acids, less so to concentrated acids. The ethylene-sulfur dioxide resin is insoluble in concentrated acids, while resins from higher olefins tend to dissolve in concentrated sulfuric and nitric acids but may be precipitated apparently unaltered. The resistance of these resins to alkali is not great. This, and the thermal instability at elevated temperatures, are the main weaknesses.

Other groups of resins utilizing sulfur have been developed by

both Texas Gulf Sulphur Company and Pure Oil Company. Petropol is the trade name of an unsaturated hydrocarbon which reacts with sulfur in the presence of oils. The resulting resins are halfway between thermosetting and thermoplastic and have possibilities as substitutes for linoleum-like materials. Application of these resins has been held back by diversion of Petropol to paint.

Another series is the Thiokol group. These resins have been made into molding compounds, although handicapped to some extent by a disagreeable odor.

Texas Gulf Sulphur Company has been carrying on considerable research to find new uses for sulfur and has been endeavoring to find a material which would plasticize sulfur and make it less brittle. It has had some success in developing a compound similar to Thiokol made by the reaction of ethylene with sulfur. A cement and joining material has been produced, made up of the following components: 54 per cent sulfur, 1 per cent Thiokol and 45 per cent inert materials such as silica and coke. This cement has been used in substantial quantities, and in 1942 the output was between 10,000 and 12,000 tons. It has been used in construction of acidproof tanks and has been substituted for lead in joining pipes. In this cement-like material either an organic or an inorganic filler may be used.

Hercules Powder Company has developed various organic fillers such as sulfurized terpenes and has taken out several patents on these materials.

Texas Gulf Sulphur Company has also spent much time and effort trying to plasticize sulfur with asphalt-like materials, but thus far not much success has been met, although efforts are being continued. These materials are potentially cheap and are considered to have possibilities for road building, casing pipe and impregnating material.

Some work has also been done on sulfurized lignins. Another development is the use of sulfur in paper impregnating plastics.

One of the latest subjects of inquiry has been the possibility of using sulfur as a filler in making molding power. If successful, it would have the important advantage in being cheaper than other fillers now used.

COMPARABLE PROPERTIES OF SOME OF THE NEW PLASTICS

	Nylon	Polyethylene	Allyl (C.R. 39)	Vinylidene Chloride (Saran)	Melamine (alpha cellulose filled)
Specific gravity	1.14	0.92	1.31	1.70	1.49
Basic color	Light cream	White translucent	Colorless	Colorless	White translucent
Tensile strength, psi	10,530	1,700	5,500	6,000	7,570
Heat distortion temperature, °F.	149	122*	131–158	150–180	410
Flammability, in./min	Self-extinguishing	Ignites and burns slowly	0.3	Self-extinguishing	Almost nil
Water absorption, %	1.5	0.01	0.2 to 0.4	Less than 0.1	0.68
Dielectric strength, v/mil	300	1,000	523	500–3,000	340
Flexural strength, psi	12,600–14,600	1,700	8,000–10,000	15,000–17,000	14,000

*Load 66 psi.

CHAPTER III

Established New Materials

MELAMINE RESINS

THE melamines are one of the latest of the thermosetting resins and consequently have not been used to so great an extent as have the phenolics and ureas. At the present time, the melamines are more expensive than the other two thermosetting resins and production capacity is limited. However, both of these conditions show considerable promise of improvement and the melamines seem destined to come into much wider use after the war.

The chemical "melamine" was originally synthesized by Liebig over a century ago. It was known for many years that melamine could be produced from calcium cyanamid, a product of the electric furnace. Melamine reacts with formaldehyde to produce a soluble and fusible resin which is colorless and water clear when obtained from pure materials. It is hygroscopic and miscible with water and water-alcohol mixtures. When subjected to heat, or under the influence of certain chemicals, it becomes insoluble, infusible and, as compared with its unconverted form, relatively tough. This change occurs over a wide range of acidity and basicity, in contrast to other thermosetting resins. The unconverted resin is capable of reacting with alcohols to form resins which are soluble in a wide variety of organic solvents. Melamine resin can be used in combination with either mineral or cellulosic fillers for molding compositions and laminated articles.

The melamine resins have found wide use during the war in electrical equipment because of their outstanding arc resistance. Such equipment must operate under conditions of service far more severe than are normally encountered in peacetime. Better insulating materials were called for and improvements in the resistance to fire, heat and the carbonizing effect of the electric arc were particularly needed. Melamine resin in its cured form will not continue to

burn after the source of heat has been removed, nor is it readily carbonized under the influence of the electric arc. In addition to these special properties it has good insulating qualities.

Melamine resins will cure in contact with heat-resistant inorganic fillers such as asbestos, glass and silica. Asbestos filled molding compounds were consequently developed and have largely replaced hard rubber and other plastics in aircraft ignition systems.

At high altitudes arcing is increased by the rarity of the atmosphere and ignition parts are often surrounded by corona discharges. Parts molded from melamine perform equally well at extremes of temperature and humidity and are not damaged by the action of nitric acid, which is formed at high altitudes.

Melamine laminated products, which possess these added advantages of arc and heat resistance, are now commercial available. For example, three commercial grades are being produced by the Formica Insulation Co. and other laminators are prepared to furnish similar products. Even the fabric base material is self-extinguishing. The glass cloth and asbestos base products are, of course, more highly resistant to heat and fire.

Paragon Plastics, Inc., has developed a melamine base molding material with mineral and asbestos fillers for use in medical instrument handles which require repeated sterilization and must be kept free from stains.

Prior to the war, melamine resins were used extensively in paper laminates to impart hardness, scratch resistance, color stability, heatproofness, and protection against the action of cleaning agents. These laminates have been used for bright colored table tops and bar tops. The manufacture of laminates for this type of application was discontinued with the advent of the war.

A similar technique has been utilized, during the war, in the production of name plates, translucent instrument panels and permanently mounted instructions and diagrams for servicing military equipment.

The heat resistance of melamine laminates, particularly in translucent form, will undoubtedly expand the use of such products in the field of lighting, and the weathering resistance imparted by

melamine will permit, after the war, the use of laminates for exterior applications.

In combination with alpha cellulose, molding compositions were developed before the war in pearl and a limited range of bright stable colors. These were used for the molding of wash buttons which, after repeated laundering, preserved their original gloss and general appearance. The alpha cellulose molding material was also found well suited to use in molding tableware, where its hardness and stain resistance were its principal advantages. Owing to its light weight, combined with relative lack of fragility, molded tableware has been utilized extensively by the Navy. More recently, a number of the molders have been producing compartment mess trays with a medium impact, fabric-filled melamine molding composition.

An interesting application of melamine has been its use in circuit breakers where it has been selected because of its resistance to shock, resistance to arcing and tracking, and its relative fireproofness. This is a type of application for which it is anticipated that there will be a considerable civilian demand.

A recent application of melamine resin has been in hot-set waterproof glues for plywood and laminated wood. Its outstanding characteristic is the strength of the glue line when under tension, and in shear, combined with water resistance far surpassing the requirements for aircraft plywood. (Melamine bonded plywood has good fungi resistance.)

The use of melamine in glues provides an excellent example of a unique property of melamine. It has been found that the addition of relatively small proportions of melamine resins to urea resins produces glues having a bonding quality much superior to that of straight urea glues. Whereas the use of urea resins without melamine addition has provided a strong bond, with limited failure, the addition of 2 per cent melamine has reduced failure in the joint to 6 per cent, and addition of 5 per cent melamine or more has eliminated joint failure entirely. Tests show 100 per cent wood failure.

Additions of melamine have also imparted to the bond the desirable characteristic of resistance to boiling water. Whereas urea resin bonded plywood has delaminated completely upon boiling in water

for 3 hr., the addition of 5 per cent melamine has provided a bond which remains intact after boiling and breaks at a shear strength of 125 lb. per sq. in., the addition of 10 per cent provides a shear strength of 260 lb. per sq. in. and the addition of 15 per cent gives 290 lb. per sq. in.

Based on this property of melamine, there have been developed and are at present marketed, melamine modified urea resin glues for hot press plywood assembly which are surpassing all requirements of Army and Navy specifications for aircraft plywood. These resins provide a bond in plywood which fails only at a high loading and exhibits very substantially 100 per cent wood failure in both shear and tension breaks.

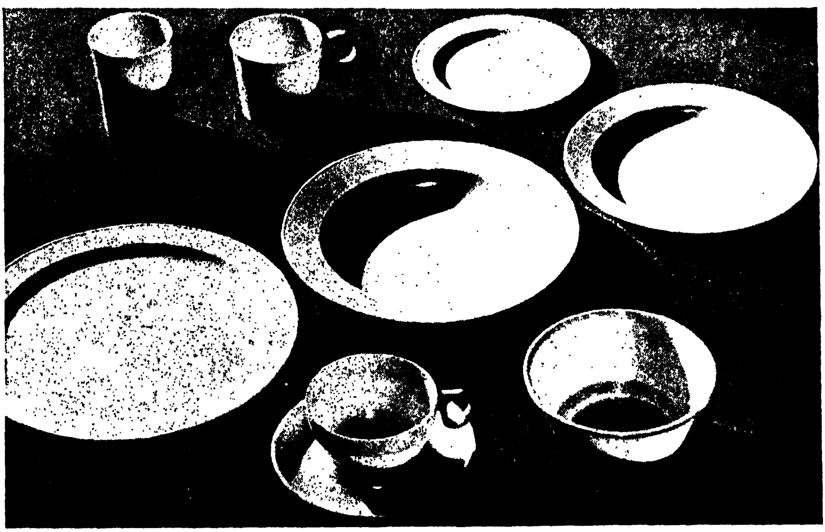
Numerous applications, other than in plastics, demonstrate the special ability of melamine when used in small proportions to impart particular properties to other products, without modifying their fundamental characteristics, texture or form.

A good example of this is paper. It has been found that when 3 per cent of a melamine resin acid colloid is incorporated in the beater in manufacturing paper, the wet-strength properties are greatly improved. In contrast with untreated paper, which scarcely holds together when wet, the one containing melamine resin is over 60 per cent as strong when wet as when dry. In addition to imparting wet strength, the addition of melamine resin greatly improves the wet rub resistance. Contrary to what might be expected, the addition of the resin does not embrittle the paper, or appreciably affect its absorptivity, but actually improves the dry tensile strength and increases many times the capacity of paper to be repeatedly folded without fracture. These improvements are retained even on prolonged storing of paper under high humidity and temperature conditions. Paper so treated has been used for toweling, blueprints, maps, heavy duty paper packaging and currency. The utilization of melamine resins in the manufacture of paper is making possible the use of paper in applications from which it has been excluded by reason of its great loss of strength upon becoming wet.

Another example of the use of melamine resins in relatively small proportions to impart specific properties is in the treatment of

textiles. These resins, in water solutions, have been used to render fabrics creaseproof, that is, to increase their resiliency, in the production of semipermanent glazed chintz, which in contrast to those glazed with starch can be laundered, as stiffening agents, and as hardening agents to modify polyvinyl butyral and other elastomers in impermeable coatings.

The alkylated melamine resins produced by reaction with alcohols have been used extensively, particularly before the war, as components of baking enamels for finishing automobiles, refrigerators, bathroom and kitchen cabinets, washing machines and numerous other metal appliances. It is expected that such uses will show a



Courtesy American Cyanamid Co.

FIG. 8. New designs and thicker sections make the Melmac tableware most attractive. The samples shown are alpha cellulose filled.

substantial increase after the war. Melamine resins contribute not only extreme hardness to these enamels, but curing speed, color retention, resistance to heat and weather and the action of many chemicals and solvents.

The versatility of the applications of melamine is demonstrated by its ability to be used in conjunction with a wide variety of materi-

als, not only plastics, but other materials which are in no way directly related to plastics. In all instances melamine imparts a high degree of resistance to the effects of water and moisture vapor. In the field of plastics, melamine imparts heat and fire resistance, arc and track resistance, hardness and general inertness to the effects of humidity and water.

Melamine is now available in various forms. There are three types of molding compounds — the alpha cellulose filled, the mineral filled and the macerated fabric filled. Only the alpha cellulose type was available before the war but the other two types are now being used in many military applications and will offer greatly expanded possibilities for functional civilian uses when the war is over. In addition, melamine is available in the form of dry resins and solutions in suitable solvents.

The principal producers of melamine resins are American Cyanamid Co. (Melmac), Plaskon (Plaskon Melamine) and Monsanto Chemical Co.

Different companies give tables of properties of melamine compounds with slightly different values. The two tables included here are typical of the range.

TABLE OF PROPERTIES

	Melmac 1077 (alpha cellulose filled)	Melmac P-3020 (chopped cotton filled)	Mineral Filled Melmac		
			592	S-6003	P-6004
Electrical Characteristics					
Arc resistance, ASTM....	125 sec	111 sec	133 sec	175 sec	186 sec
Tracking resistance.......	Excellent	Good	Excellent	Fair	Excellent
Dielectric strength, ASTM (Room temperature)......	340 v/mil	270 v/mil	535 v/mil	440 v/mil	470 v/mil
Power factor, 60 cycles....	3.7%		10%	11%	14%
Dielectric constant, 60 cycles..............	7.9		7.7	8.5	10
Power factor, -10^6 cycles ASTM..............	2.9%	4.1%	3.8%	2.8%	4.4%
Physical Characteristics					
Specific gravity..........	1.49	1.4	1.7	1.98	1.98
Weight per cu. in.........	26 gm	25 gm	26.2 gm	30.8 gm	30.78 gm

TABLE OF PROPERTIES (*Continued*)

	Melmac 1077 (alpha cellulose filled)	Melmac P-3020 (chopped cotton filled)	Mineral Filled Melmac		
			592	S-6003	P-6004
Impact-Izod ft/lb	0.26	0.686	0.326	0.308	0.325
Flexural — ASTM, lb/psi	14,000	14,000	9,280	9,180	11,180
Tensile strength, ASTM, psi	7,570	7,000	5,900	5,920	6,620
Coefficient of expansion, +15°C	44×10^{-6}		37×10^{-6}	22×10^{-6}	22×10^{-6}
Heat distortion	410°F		266°F	266°F	410°F
H_2O absorption, ASTM	0.68%	1%	0.13%	0.07%	0.07%
Shrinkage-mold, in./in.	0.005–0.007	0.003–0.004	0.006	0.0057	0.0054
After 8 hr at 220°F	0.004–0.005	0.002–0.003	0.001	0.002	0.0029
Heat resistance, ⅛ in. test piece	210°F	220°–250°F	300°F	375–400°F	300°F
Raw Material Characteristics					
Particles size	Powder and granule	Chopped cotton cloth	Pass ⅛ in. screen	Pass ⅛ in. screen	Pass ⅛ in. screen
Apparent density	0.70 gm/cc		0.74 gm/cc	0.95 gm/cc	0.85–0.90gm/cc

TABLE OF PROPERTIES (*Continued*)

	Melmac 1077 (alpha cellulose filled)	Melmac P-3020 (chopped cotton filled)	Mineral Filled Melmac		
			592	S-6003	P-6004
Pourability	Excellent	Poor	Good	Good	Good
Recommended molding pressure compression	2000–4000 psi	2000–6000 psi	1000–6000 psi	1000–5000 psi	1000–5000 psi
Transfer		10,000–30,000 psi	6000–20,000 psi	6000–20,000 psi	4000–20,000 psi
Molding temperature	300–340°F	275–330°F	280–360°F	265–365°F	265–365°F

CHEMICAL RESISTANCE OF MELMAC 1077 (ALPHA-CELLULOSE FILLED)

No change after 12 weeks immersion of 25°C in the following:

Tap Water	Dioxane	Ethylene Dichloride	Xylene
10% Citric Acid	Methanol	Acetone	Liquid Soap
10% C.P. Caustic	Butyl Cellusolve	Glycerin	0.5% Ivory Soap Solution

7.3% Aluminum Chloride Solution

Concentrated Ammonia causes slight yellow discoloration.

40% Sulfuric Acid — 1 week at 40°C — Bad discoloration and attack on surface.

PROPERTIES OF PLASKON ALPHA CELLULOSE FILLED MELAMINE MOLDING COMPOUND

Molding qualities	Excellent
Compression molding temperature °F	280–340
Compression molding pressure, psi	1500–6000
Compression ratio	2.5–2.7
Mold shrinkage, in./in.	0.010–0.015
Specific gravity	1.45–1.55
Specific volume, cu. in./lb	18.6
Flexural strength, psi	10,000–16,000
Impact strength, ft-lb/sq in. of notch, 1/2 × 1/2 in. notched bar, Izod test	0.24–0.35
Resistance to heat, °F (continuous)	210
Softening point, °F	None
Volume resistivity, ohm-cms (50% relative humidity and 25°C)	12^{12}–10^{13}
Dielectric strength, short-time v/mil, 1/20 in. thickness	640–690
Dielectric constant, 60 cycles	8.6–9.4
Dielectric constant, 10^6 cycles	3.5–7.6
Power factor, 60 cycles	0.05–0.07
Power factor, 10^6 cycles	0.05
Burning rate	Nil
Effect of age	None
Effect of sunlight	Slight color change
Effect of weak acids	None
Effect of strong acids	Decomposes
Effect of weak alkalies	None
Effect of strong alkalies	Attacked
Effect of organic solvents	None
Effect on metal inserts	Inert
Machining qualities	Fair
Clarity	Translucent
Color possibilities	Unlimited

POLYVINYL ALCOHOL RESINS

Polyvinyl alcohol resin has come into prominence during the war period as a replacement for crude rubber. It has been made in quantity only since 1941. The resin is characterized by oil and grease resistance and by toughness.

It now is being molded into tubing and gaskets for airplanes, trucks and other military equipment, where it has proved superior to rubber because of its high resistance to oils. Aprons and gloves for workers handling oil, solvents and grease and food packages are made from this plastic. It is used in making plastics printing plates,

greaseproofing paper, sizing textiles and military applications.

Plasticized polyvinyl alcohol can be molded into tough, elastic, rubber-like articles with outstanding resistance to the action of solvents, oxygen, light, heat and vibration. By varying the grade of polyvinyl alcohol and the type and amount of plasticizer, it is possible to prepare a wide range of compositions suitable for molding or extrusion in conventional rubber and plastics equipment. Polyvinyl alcohol resins are unaffected by oils, fats, greases and other common organic solvents such as alcohols, esters, ethers, ketones and both aliphatic and aromatic hydrocarbons. Through a proper selection of suitable plasticizers, molded products may be produced which are also highly resistant to organic solvents. Articles molded from polyvinyl alcohol are not recommended where a high degree of water resistance is required. They soften, swell and lose strength on prolonged exposure.

The resin has promise as tubing, film or a coating material. Gasoline and oil hose lines are applications suitable for this tough, oil- and grease-resistant plastic. E. I. du Pont de Nemours & Company, Inc., has played a prominent part in development of the polyvinyl alcohol resins.

POLYVINYL ACETATE IN EMULSION

Polyvinyl acetate in emulsion is a new and relatively little known plastic. It has been used during the war as a rubber latex substitute or extender, replacing, for example, large quantities of rubber latex in mid-soles for shoes. It has also been used in the fabrication of gas-proof fabrics and as an adhesive. Polyvinyl acetate may be used in increasing quantities after the war as a replacement for rubber latex and as an adhesive.

NEW FURANE RESIN

The U. S. Stoneware Company has announced a new resin, Duralon, which is a furane derivative, characterized by exceptionally low water absorption. It is insoluble (after activation) in almost any solvent or combination of solvents, has good electrical properties and has stability in storage and handling.

Duralon resin, in its pure form, is a heavy, viscous liquid, dark

maroon in color. On incorporation of catalyst and application of mild heat, it reverts to an extremely hard, dense, black substance. Varying physical, chemical and electrical properties can be developed in the base resin by incorporation of the usual fillers and lubricants. In certain stages it can be readily machined by drilling, milling, turning, sanding or grinding.

The resin is readily soluble, before activation, in many inexpensive hydrocarbons, as well as in ketones and chlorinated solvents.

Preliminary studies indicate that it possesses definite molding possibilities, but its paramount immediate importance is as an impregnant, as a laminating and bonding agent, or as a protective coating material. It is in these applications that its resistance to moisture, its insolubility in solvents (even at elevated temperatures), its versatile surface characteristics (ranging from a high gloss to a crinkle finish), prove valuable. Many of these properties can be attributed to the unusual wettability of the unconverted resin.

Duralon solutions may be applied as coatings by any of the conventional processes, or they may be used for impregnation of porous materials such as stone, cement, plywood, asbestos, glass fibers or other fibrous materials, or as a bonding agent for abrasive compounds, powdered metals, etc., or for adhesive bonding of fibrous materials to each other.

Prior to the application of heat, Duralon coatings are soft and flexible. As heat is applied (a mild bake is usually sufficient), the coatings remain thermoplastic up to a point, at which time they become increasingly thermosetting, depending upon the type and extent of activation. Other Duralon resins, to be made available, are completely nonthermosetting and have interesting plasticizing, wetting and tackifying properties over wide temperature ranges.

No particular surface preparation is needed before application of Duralon coatings, nor is a prime coat necessarily required.

The coatings, after baking, are hard and, though somewhat more brittle than coatings of the thermoplastic type, show excellent abrasion resistance and utter lack of aging characteristics. The water and solvent resistance of the pure resin is fully imparted to coatings made from the resin. Such coatings show practically zero water absorption, are unaffected by any solvent, possess excellent resist-

ance to all nonoxidizing acids, and good resistance to alkaline materials. Products made from these resins not only show a permanence of properties at normal temperatures but apparently retain a preponderance of their desirable properties at temperatures in excess of 400°F.

THE ALLYL RESINS*

The allyls are a distinctly new type of plastic derived from allyl alcohol. This alcohol is produced by Shell Union Oil Corp. and also by Carbide and Carbon Chemicals Corp. The 1944 price of allyl alcohol was $0.35 per lb. but it will probably be reduced substantially when large-scale commercial production is attained.

The resins show unusual promise as colorless, transparent, thermosetting, synthetic materials. They possess the common characteristic of forming insoluble, infusible, polymeric products through pure polymerization rather than condensation reactions such as are characteristic of the conventional thermosetting resins. The group covers a wide range in reactivity, hardness, strength, flexibility and general resistance to deteriorating influences. Variations in properties are achieved, not by the addition of plasticizers, but by adjustment of the chemical structure of the molecules of the resin monomer.

Some of the allyl resins are about the nearest thing to glass that has yet been developed in the field of plastics, and they have a much greater surface hardness than other transparent plastics. Although they will probably not displace flat plate glass, they may be used in place of some curved sections and of safety glass. Two of the large glass companies, Pittsburgh Plate Glass Company and Libbey-Owens-Ford Glass Company are interested in the development of these resins which may also have possibilities in the laminating field.

The first allyl type resin, CR-39, was introduced by the Columbia Chemical Division of Pittsburgh Plate Glass Company in 1941. Other companies now interested in these resins include the Plaskon Division of Libbey-Owens-Ford Glass Company, Continental Can Company, General Electric Company and Monsanto Chemical Company. Considerable information has been released about

* See page 177 for MR allyl resins.

CR-39, the first of these resins. Its properties as a typical allyl type resin follow.

Monomeric CR-39 is a clear, colorless, water-insoluble, organic liquid of low viscosity, containing carbon, hydrogen and oxygen. It is stable for long periods at ordinary temperature, but, upon heating in the presence of a catalyst, such as benzoyl peroxide, it changes into a sirupy stage, after which it gradually increases in viscosity and then forms a gel. Upon application of further heating, the gel hardens and finally becomes a strong, hard, infusible, clear, substantially colorless solid. The monomer is thus converted into a thermohardened resin by a simple polymerization process without the evolution of water, ammonia or any other by-product. This absence of by-products, together with the inherently low volatility of the monomer, makes possible its use in fabricating processes without the application of high pressures.

CLEAR CAST SHEETS. Pure CR-39 is cast-polymerized under suitable conditions into transparent sheets. Compared with other

Courtesy Pittsburgh Plate Glass Co.

FIG. 9. Flat and bent sheets of transparent CR-39.

transparent plastics, it offers the advantages of extraordinary resistance to chemicals and solvents, of greatly increased abrasion and mar resistance, of not crazing when held under stress and of much greater resistance to distortion and flow under heat. It compares well with other transparent plastics in specific gravity,

strength, shock resistance and ease of forming into simple bent shapes. It can also be formed into moderately compound curved shapes but is not adapted to deep drawing. Cast CR-29 sheets burn at only one-third the rate of cast acrylates. CR-39 sheets are extraordinarily clear and weather resistant but have a tendency to become slightly yellow upon prolonged weathering. The small discoloration that occurs is not accompanied by any substantial decrease in clarity or light transmission; however, CR-39 is superior to other transparent organic plastics both in resistance to surface abrasion in glazing applications and in resistance to actual wear. The resin is many times as resistant to marring by rubbing (Taber method) or by impinging (falling emery) abrasive particles than, for example, the methacrylate plastics. It is much less resistant to the rubbing (Taber) type of abrasion than glass but is approximately as resistant as glass to falling emery abrasion.

In bursting strength (ability to withstand gas pressure over large areas), breaking strength (ability to withstand a falling steel ball) and shock resistance as measured by impact tests, CR-39 sheets compare favorably with the methacrylate plastics.

CR-39 has good photoelastic properties. It does not exhibit any optical creep, that is, when the load is removed no part of the stress pattern remains, up to nearly the ultimate strength of the material. The optical sensitivity (86.6 lb. per sq. in. per fringe per inch thickness) compares well with other photoelastic materials, and the fringes are more distinct.

In common machining operations, such as sawing, turning and drilling, some of the unique physical characteristics of CR-39 are noticeable. When suitable tools and methods are employed, all these operations may be performed without difficulty. The infusibility of CR-39 facilitates operations in which heat is developed, such as sawing, sanding, grinding, polishing and buffing. These operations may be performed without the tendency found in some conventional thermoplastics to drag, fuse or gum.

Fully cured sheets of CR-39 can be formed at elevated temperatures to fairly severe simple curvatures and moderate compound curvatures. The sheets are not capable of being drawn over large areas, however. The forming temperature lies between 95° and

105°C. (200° and 220°F.), and there is no advantage in raising it. Conventional plastics forming equipment is used. CR-39 sheets show little tendency to distort or to develop surface defects in heating and forming operations and they are not easily damaged by overheating in the oven. The formed sheets have some tendency to lose curvature, but this may be minimized by retention in a light frame.

LAMINATING. CR-39 is applicable to low-pressure laminating, because it cures without evolution of any volatile by-product and also because it exists as a liquid of low viscosity with high penetrating power, thus requiring no solvents or diluents. Base materials such as fabrics, felts, papers and wood can be impregnated readily with monomeric CR-39 containing a suitable catalyst and cured into laminated objects of high strength by moderate heating, normally at 70° to 115°C. (162° to 239°F.), with the application of no more pressure than is required to hold the layers in intimate contact with one another. This pressure ranges from 0.01 to 10.0 lb. per sq. in., but for most applications it is between 1 and 2 lb. per sq. in.

CR-39 monomer may be stored in steel drums and has been kept in storage at ordinary temperatures for periods in excess of four months without significant change. Because no inhibitors are required for stabilization of the monomer, distillation or washing operations to remove inhibitors prior to use are unnecessary. Catalysts are incorporated readily owing to the low viscosity and good solvent power of the monomer, and the resulting solution containing catalyst may be kept several days at ordinary temperatures before an increase in viscosity due to polymerization becomes noticeable. Because of its low volatility, CR-39 monomer possesses almost no odor at the ordinary temperatures of laminating operations and only slight odor at normal curing temperatures. The volatility is sufficiently low to permit vacuum bag and other vacuum techniques to be employed without bubbling or appreciable evaporation of the resin monomer.

Polymerization of CR-39 is inhibited by metals such as copper and lead, by sulfur or sulfur compounds such as are present in

vulcanized rubber and also by atmospheric oxygen. These materials should therefore be absent during polymerization.

The allyl type of resin offers interesting possibilities in decorative laminates because of its transparency, virtual colorlessness and high resistance to wear, abrasion and attack by chemicals and weather. The monomeric liquid nature of the material, however, will necessitate development of special methods for use, differing from those now employed in working with conventional laminating varnishes, which are solutions of more or less solid resinoids.

Fabrics can be impregnated by simply brushing the monomer — either successive layers as they are piled up or the assembled laminate of several thicknesses.

The principal precaution to be observed is the elimination of air bubbles from all interfaces. Flat laminated sheets can be cured between plates of glass, metal or plastic with no more pressure than the weight of the top plate. Curved shapes can be made either by forming laminates according to the technique employed in shaping clear sheets or by curing the original laminate in the desired shape. The latter method is preferable if form stability is required and if no means is available for restraining the slight tendency of bent sheets to spring back to their original flat form.

For laminating shaped objects, inexpensive molds of plaster, papier-mâché, cardboard, sheet metal, concrete, cast metal, wood, glass or combinations of any of these materials can be used. The slight pressure needed to hold the plies in intimate contact can be applied (a) by screw clamping, (b) by wrapping tightly with dry fabrics, (c) by applying bags filled with shot as weights, (d) by wrapping the cellophane-covered laminate with rubber tape under slight tension, (e) by use of rubber bags either inside a female form and inflated to a few pounds per square inch or as envelopes around a male form and evacuated so as to utilize atmospheric pressure on the laminate, or (f) by clamping together two rigid mold parts, one of which is cushioned by sponge rubber or by some other means. The best results are obtained when one of the mold walls is rigid and the other flexible to allow for irregularities in section, overlapping of the fabric layers, etc.

PHYSICAL PROPERTIES OF CR-39 — PAPER LAMINATES

Paper	Kraft		Hurlbut 716 (Rag Paper)		Mitscherlich (Spruce Sulfite)	
Direction of Test (w)	Parallel	Perpendicular	Parallel	Perpendicular	Parallel	Perpendicular
Properties						
Tensile strength, psi	21,600	10,700	12,200	11,200	25,600	10,400
Flexural strength, psi	22,600	17,400	18,400	16,800	25,800	16,400
Modulus of elasticity, psi × 10^5	11.9	7.8	9.4	8.0	20.9	8.2
Compressive strength, (edgewise), psi	14,500	13,600			14,100	12,900
Impact strength, ft-lb, notched Izod	0.91	0.6	1.0	1.0	1.1	0.90

COMPARISON OF CR-39 WITH PLATE GLASS AND METHYL METHACRYLATE

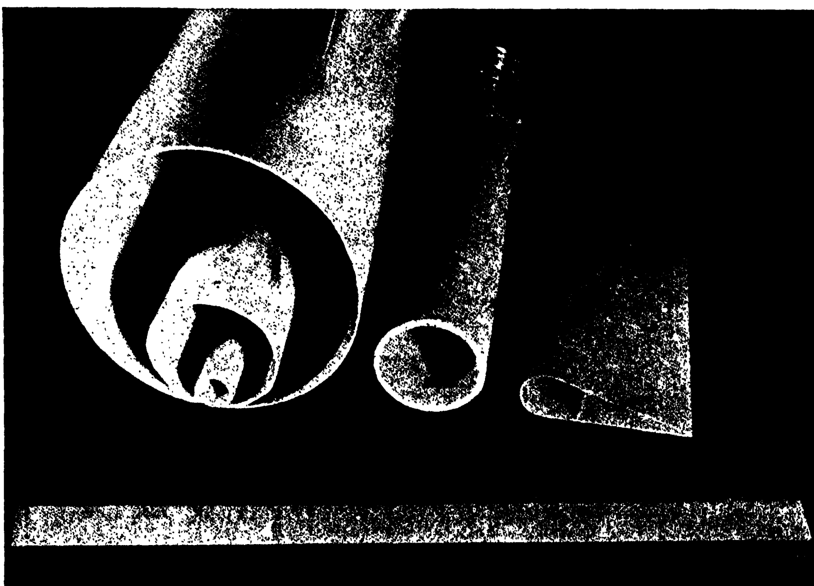
Properties of Polymer	CR-39-1	Methyl Methacrylate	Plate Glass
Specific gravity (25°C/4°C)....	1.31	1.19	2.5
Refractive index (20°C).......	1.50	1.49	1.52
Hardness			
Knoop....................	15–18	18–20	Approx. 400
Rockwell, M scale..........	95–100	85–105	..
Cold flow			
Barcol impressor, 15 sec.....	8–11	13	None
Plastic yield			
(1000 lb ½-in. cube, room temperature)..............	0.006 in.	0.005 in.	None
Abrasion resistance, mar resistance, falling emery.........	8–10	1	10
Tensile strength, 25°C psi......	5,000–6,000	7,500	6,500
Flexural strength, psi			
122°F....................	5,000–6,000	9,000–11,000	6,500
77°F.....................	8,000–10,000	13,000–15,000	6,500
Modulus of elasticity in flexure, psi $\times 10^5$			
77°F.....................	2.5–3.3	3.7–4.5	100–110
Thermal expansion			
linear coefficient per °C $\times 10^{-5}$			
−10°C to +25°C..........	8.7	8.1	0.8
Thermal conductivity			
Btu/hr/ft²/in./°F...........	1.45	1.16	6.67
Maximum recommended operating temperature under no load			
Continuous service..........	176°F	158°F	..
Intermittent (1 hr duration)..	302°F	176°F	..
Burning rate, ⅛-in. sheet			
Navy test, in. per min.......	0.3	1.1	0
Light trans. after aging			
White (%)................	89–91	90–91	..
Water absorption (%)	0.2–0.4	0.3	..

Fully cured laminated sheets can be cemented together by use of monomeric CR-39 if the areas to be bonded are thoroughly roughened. A second heat-treatment is necessary to cure the bonding monomer, but this apparently has no injurious effect on the rest of

the laminate. Reheating is usually carried out in an oven. Other adhesives are being developed to reduce the time required for cementing operations.

Most of the important properties of cured CR-39 laminates are dependent primarily on the nature of the base material used, the influence of the resin being of secondary importance. This is true of such properties as tensile strength, impact resistance and density. Other properties, such as compressive and flexural strengths and solvent and water resistances, reflect more strongly the influence of the resin.

APPLICATIONS. Because of its great fluidity CR-39 is not well adapted to use in paints; the time required for its polymerization



Courtesy Pittsburgh Plate Glass Co.

FIG. 10. Shaped laminates made with Allymers (CR-39).

(of the order of hours depending on the mass) and the inhibition of polymerization by air render it unsatisfactory for finishing processes for paper or fabrics where polymerization must be rapid and occur in the presence of air.

An important point is that shrinkage amounting to 14 per cent in volume occurs during polymerization of CR-39. Special molds capable of accommodating this shrinkage must therefore be employed in casting, if dimensions and shapes are to be reproduced accurately. The shrinkage in CR-39 and its relatively slow polymerization also make it unsuitable in its normal forms for molding or die casting.

New Columbia resins to overcome limitations in CR-39 are now in the experimental stages. One of these, CR-149, is in commercial production. The name Allymer has been suggested by the Columbia division to cover all its allyl alcohol resins.

VINYLIDENE CHLORIDE POLYMERS

The French chemist Regnault in 1838 reported a strange new fluid that was later determined to be unsymmetrical dichloroethylene, now more commonly known as vinylidene chloride. It was not until recently, however, that this material received much attention. In 1922, B. T. Brooks found that halogenated ethylenes other than vinyl chloride and vinyl bromide show a tendency toward polymerization. Staudinger and Feisst reporting in 1930 in connection with the polymerization of an apparently impure unsymmetrical dichloroethylene indicated that the liquid polymerizes quickly in the light or slowly in the dark.

This polymeric material is completely saturated, and its structure is represented by the long chain

$$—CH_2—CCl_2—CH_2—CCl_2$$

Feisst found that the polymer is crystalline and this was later confirmed by G. Natta and R. Rigamonti.

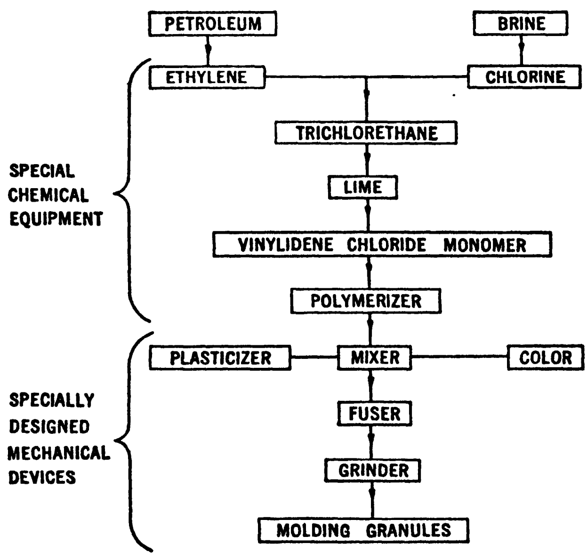
Development of vinylidene chloride by the Dow Chemical Company began over a decade ago. Its research men investigated the material while working on chlorinated aliphatic compounds. A comprehensive program of research on vinylidene chloride was subsequently carried out and it was introduced commercially by Dow early in 1940 under the trade name Saran.

Chemical and Physical Structure. The raw materials for vinylidene chloride are petroleum and brine. Ethylene, made by

cracking petroleum, and chlorine from the electrolysis of brine, combine to form trichloroethane, which is converted into vinylidene chloride. The resulting material is a clear colorless liquid having a boiling point of 89°F. and a structural formula $CH_2{=}CCl_2$.

Vinylidene chloride can be readily polymerized to form a long, linear, straight-chain polymer. By selection of copolymers and control of the polymerization conditions, polymers may be formed that have softening points ranging from about 158°F. to at least 356°F.

Materials ranging from soft and flexible to hard and rigid can thus be obtained. The commercial polymers now in use have softening points from 248° to 284°F., with a molecular weight of approximately 20,000. These polyvinylidene chloride plastics are best known by their trade name, Saran.



Courtesy Dow Chemical Co.

Fig. 11. Flow sheet for the production of vinylidene chloride.

Unlike most organic thermoplastics, which exist in an amorphous state, Saran exhibits regions of crystal structure, readily demonstrated by its X-ray diffraction pattern. Saran can be made amorphous under special conditions. When allowed to return to room

temperatures, it gradually changes to its normal crystalline state. It can be converted by mechanical working from an amorphous to an oriented crystalline state.

The three physical states of Saran, amorphous, normal crystalline and oriented, are indicated when viewed through crossed polaroids.

PROPERTIES. While Saran can be obtained in a wide range of properties, Dow has selected a typical formulation having the general properties shown in Table I.

Saran has high resistance to chemicals and solvents. At room temperature, it is resistant to all acids and to all common alkalies except concentrated ammonium hydroxide. When it is exposed to concentrated sulfuric acid or caustic over long periods, a slight discoloration with little change in mechanical properties occurs. It is generally unaffected by both aliphatic and aromatic hydrocarbons, alcohols, esters, ketones and nitroparaffins. It is swelled or softened only by oxygen-bearing organic solvents such as cyclohexanone and dioxane. Resistance to chemicals or solvents decreases as temperature rises. The resistance of Saran to any chemical is due in part to crystallinity of the polymer. It is chemically more resistant in the crystallized than in the amorphous form.

Saran has extremely low water absorption and vapor transmission. According to one test made over a period of 24 hr., it showed almost no water absorption. This accounts for its dimensional stability and freedom from warpage over a wide range of moisture exposure conditions.

Saran is thermoplastic and has a definite softening point which limits the temperature at which it can be used. Since the softening point changes with the composition, the upper limit of operating temperature can be varied from 150°F. or lower to 250°F. Exposures to much higher temperatures are not dangerous, however, since Saran is not flammable.

The basic polymers are odorless, tasteless and nontoxic. Their high refractive index enhances their many color possibilities, and they have toughness and high abrasion resistance. Retention of these properties upon aging ensures excellent wearing qualities.

APPLICATIONS. Saran can be fabricated by conventional thermo-

plastic practice and, because of its normal crystalline structure, can be worked by various methods.

It is adapted to conventional extrusion processes. Modified screw-type extrusion equipment is used. Although modifications are minor, they are necessary for successful extrusion of Saran. Designs permitting streamline plastic flow are desirable. Since iron and copper base metals catalyze the thermal decomposition in zones above 266°F., it is necessary to select other suitable metals for such elevated temperatures. Metals that can be used in contact with Saran above 266°F. are magnesium alloys, nickel and nickel base alloys such as Z nickel, Hastelloy B, Stellite 19 and impervious hard nickel plate.

Extrusion of Saran involves maintenance of a uniform rate of feed to the screw machine hopper, mixing and heating the material as it is forced along by the screw and then forming it as it passes through the die. The extruded shape may be cooled and subsequently heat-treated.

Saran may be fed to the extrusion unit as a powder or as granules. The powder presents no bulk problem with the screw machine and eliminates a costly milling operation. The powder is manufactured, plasticized, pigmented and colored by ball milling.

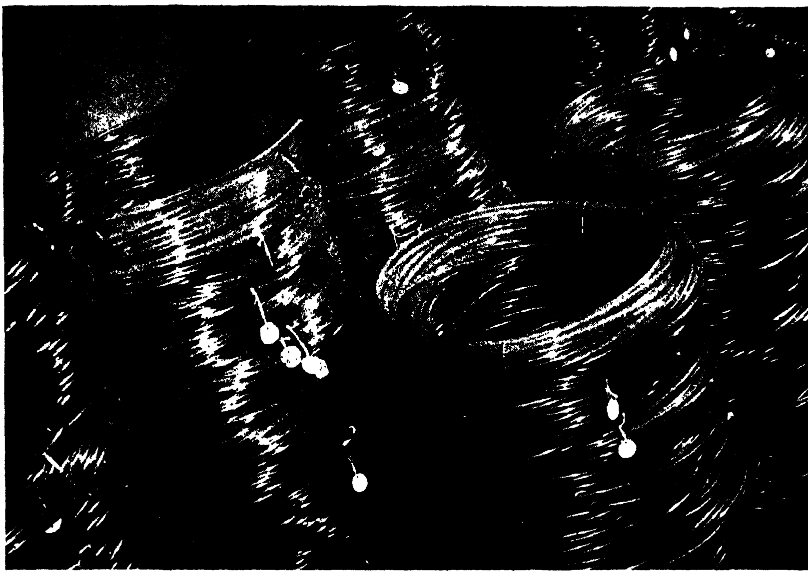
Thorough melting is of prime importance in extrusion of Saran. To accomplish this, it is necessary to heat the material to above its crystallite melting point. In this condition the product becomes completely amorphous.

Saran has a narrower softening range than most other thermoplastic materials. When it is heated above this, it can be extruded in a fluid state. Under these conditions, no plastic memory is encountered, and the desired shape and surface may be retained.

The product, when first extruded and cooled, is soft, weak and pliable. If allowed to remain at room temperature without further treatment, it gradually hardens while partly recrystallizing at a slow rate with a random crystal arrangement. By heat-treatment, recrystallization can be produced at controlled rates. Recrystallization time can be regulated from a few seconds to several weeks. For any one formulation, the rate of recrystallization varies with the temperature. Specific gravity increases during recrystallization.

A range of properties can be obtained by control of extrusion and heat-treatment. Tensile strengths may be obtained from 4000 lb. per sq. in. to 12,000 lb. per sq. in., hardness from 60 to 95 (Rockwell Superficial 15Y), elastic elongations from 10 to 40 per cent. Such products have good fatigue life.

Some of the applications of extruded Saran are as follows: rods for making gaskets, valve seats, ball checks, medicinal probes,



Courtesy Dow Chemical Co.

FIG. 12. Vinylidene chloride tubing is finding a wide market. This shows coils of Saran ready for shipping.

chemically resistant flexible tubing and pipe, tape for wrapping joints, chemical conveyor belts, screen filaments, tape and strips for die cutting and various items of wearing apparel.

The second method of fabrication of Saran is injection molding. This makes possible production of intricate shapes having properties similar to those obtained by extrusion. Equipment consists of the standard conventional type injection-molding machines modified only as to contact metals and designs through the heating tun-

nel or cylinder. The fundamentals of design include the same contact metals as listed for extrusion, strict streamlining, and reduction in thickness of plastic sections in the heating zone. Conventional injection-molding die designs and die metals can be used.

Injection molding of Saran is unique. With other commercial thermoplastics, the use of cold dies hastens the cooling of the plastics part and shortens the cycle, but the reverse is true with Saran. Cold dies produce soft, flexible, amorphous pieces. Rapid hardening is accomplished by heat-treatment in heated dies producing recrystallization. For normal sections, this permits short cycles. When heavy sections are involved, heated dies allow the section to retain its heat and thus permit rapid recrystallization. Under these conditions, Saran can be ejected from the die at temperatures as high as 212°F. in a strain-free, warp-free, dimensionally stable form. This promotes rapid cycles with heavy sections. Moldings have been produced with ¼ in. sections in a 17 sec. cycle.

Injection-molded Saran has played an important part in the war program. Many of its applications have been replacements of metals rather than of other thermoplastics. Saran has often been the only material that would satisfy the industrial requirements for the replacement of such strategic materials as nickel, aluminum, stainless steel and rubber in applications requiring chemical resistance. Some of these wartime applications have been spray-gun handles, valve seats, acid dippers, and moldings for the rayon industry, including spinneret couplings, gasket holders, filter parts, nozzle tips, rollers, guides, etc.

Good mechanical characteristics, range of attractive colors and other properties adapt Saran for use in injection molding.

Saran, like other thermoplastic materials, can be compression molded. Unlike them, however, it requires the selection of metals for dies that were listed for high temperatures in extrusion equipment. As with other thermoplastics, injection molding is usually more economical than compression molding.

The third method of fabrication, that of crystal orientation, brings out new properties of Saran. The oriented form is produced by extrusion and subsequent plastic deformation, as by stretching and heat-treatment. It is thus possible to obtain long, continuous

extrusions of monofilaments, tapes and other shapes which have exceptional properties. Although the method is not complex, it requires special control and careful attention to techniques. A brief description of equipment and techniques is as follows:

To produce strong continuous sections, the plastic must be uniformly heated to a temperature above its crystalline melting point and thereafter cooled below that point. Preferably the material is mechanically formed to a shape similar to that of the section desired before being cooled. The screw-type extrusion machine already described may be used for fusing and shaping the material, which may then be cooled to room temperature and will remain in the amorphous or supercooled conditions for a sufficient period of time to permit cold-working operations to be carried out. Saran is then ready for orientation.

The orientation process provides a method of effecting a plastic deformation and partial recrystallization of the shaped, supercooled material. The method involves an accurately controlled, predetermined rate of withdrawal of the plastic from the extrusion unit. Ultimate size and uniformity of the continuous section are regulated by controlling the withdrawal rate.

The shaped, supercooled material is then elongated under controlled conditions, suitably at room temperature. During this mechanical stretching, there is a partial recrystallization and orientation of the crystallites along the major axis of the strand. Reduction in cross-sectional area is approximately proportional to the elongation that takes place. The material may be heat-treated after or during stretching to affect the degree of crystallization and thus control the properties of the oriented article. After winding and packaging, the plastic strand is ready for use.

This method produces orientation in a single direction with resulting and unidirectional properties. These properties of high tensile strength, great flexibility, long fatigue life and good elasticity are particularly desirable for small monofilament sections where the load is along the longitudinal axis. In larger, noncircular sections, such as tapes, ovals and semicircles, the desired degree of transverse orientation can be obtained and accompanying transverse properties controlled through the introduction of other factors in the con-

tinuous process. For example, a rolling operation incorporated after the quenching step produces some flattening and transverse elongation of the strand with a resultant increase in transverse strength. Other processes involving mechanical or recrystallization control are available for desired modifications of directional properties. A variety of continuous sections can be produced as the results of range of plastic formulations and flexibility of processes.

Extruded and oriented sections have been produced for textile uses, ranging in size from 0.007 to 0.100 in. in circular monofilaments and other shapes having maximum dimensions up to 0.200 in. These materials have proved their adaptability to standard textile operations and have been fabricated by braiding, weaving, knitting and twisting. Although there are already many uses for monofilaments in the sizes commercially available, still greater fields may await single and multiple fine fibers having the properties of oriented Saran.

The monofilaments have been used to take the place of such imported natural products as hemp, long fiber paper, reed, rattan, horsehair, Spanish silkworm gut and linen. It is believed that some of these substitutes may be permanent. Some of the typical applications are the following:

1. *Filter Fabrics.* Saran's extreme chemical resistance suits it for this use. Since it is thermoplastic, the question of upper operating temperature limits immediately arises, but even at a temperature above that of boiling water, it still retains half its original tensile strength. Normal strength is recovered on cooling to room temperature.

2. *Special Ropes.* Here its high wet strength and its resistance to chemicals and fungi have proved of value in special ropes and cores for wire ropes.

3. *Articles of Apparel.* Its general attractiveness and range of color possibilities fit Saran for such apparel accessories as belts, suspenders, handbags and shoes.

4. *Upholstery Fabrics.* Its principal qualifications for upholstery fabrics are long life, ease of cleaning, abrasion resistance and flexibility, as well as color possibilities.

5. *Household Screen.* Successful use of Saran for screens for the

armed forces in the South Pacific indicates that this may be one of the most important applications of this material.

In addition to the methods of fabrication mentioned, other operations based on Saran's combination of thermoplasticity and crystallinity have been used in forming the plastic. These operations include drawing, forging, blowing, rolling, stamping and welding.

TABLE I. GENERAL PROPERTIES OF A SARAN FORMULATION

Effect of weak acids	None
Effect of strong acids	Darkens in H_2SO_4 — others none
Effect of weak alkalies	None
Effect of strong alkalies	Affected by NH_4OH, darkens in caustic, others none
Effect of organic solvents	Highly resistant
Water absorption, ASTM D570-40T	Less than 0.1%
Water permeability	Very low
Burning rate	Self-extinguishing
Thermal conductivity	2.2×10^{-4} cal/sec/sq cm/°C/cm
Specific heat	0.316 cal/°C/gm
Index of refraction	1.61
Specific gravity	1.70
Volume resistivity, dc	10^{14} - 10^{16} ohm-cms
Dielectric strength, 60 cycles	500–3000 v/mil
Dielectric constant, 60 cycles	4
Power factor, 60 cycles	0.03-0.08
Effect of age	None
Effect of sunlight	Slight
Machinability	Good
Color possibilities	Extensive

TABLE II. PROPERTIES OF MOLDED SARAN B-115

Extrusion temperature	Up to 375°F
Injection molding temperature	300°–350°F
Injection molding pressure	10,000–30,000 psi
Compression molding temperature	250°–350°F
Compression molding pressure	250-5000 psi
Mold shrinkage (injection molded)	0.008–0.012 in./in.
Specific gravity	1.68–1.75
Refractive index nD	1.61
Tensile strength	4000–8000 psi
Elongation at yield point	15–25%
Modulus of elasticity tension	$0.7–2.0 \times 10^5$ psi
Flexural strength	15,000–17,000 psi
Compressive strength at yield point	7500–8500 psi

TABLE II. PROPERTIES OF MOLDED SARAN B-115 — *Continued*

Impact strength	
½ in. × ½ in. notched bar, Izod	2–8 ft-lb/in.
Thermal conductivity	2.2×10^{-4} cal/sec/cm²/°C/cm
Specific heat	0.32 cal/°C/gm
Thermal expansion	15.8×10^{-5}/°C
Resistance to heat (continuous)	170°F, approximately
Resistance to heat (intermittent)	212°F
Softening point	240°–280°F
Distortion point	150°–180°F
Volume resistivity	
(50% relative humidity and 25°C)	10^{14}–10^{16} ohm-cm
Breakdown voltage, 60 cycles, instantaneous	
0.125 in. thickness	500 v/mil
0.020 in. thickness	1500 v/mil
0.001 in. thickness	3000 v/mil
Dielectric constant, 60, 10^3 and 10^6 cycles	3–5
Power factor, 60, 10^3 and 10^6 cycles	0.03–0.15
Water absorption, ASTM, D570–40T	Less than 0.1%
Burning rate	Self-extinguishing
Effect of age	None
Effect of sunlight	Darkens slightly
Effect of acids, alkalies, solvents	None to slight
Effect of metal inserts	Inert
Machining qualities	Good
Welding ability	Unexcelled
Clarity	Translucent to opaque
Color possibilities	Extensive
Hardness: Rockwell Superficial	15Y, 65–95
Durometer A	Above 95
Rockwell M	50–65

GOODRICH GEON RESINS

The Geon resins are thermoplastic in nature and are of several types. Geon 100 series resins are special polymers of vinyl chloride characterized by their thermal and light stability, toughness and chemical inertness. Geon 101 is designed for electrical applications. Geon 102 is adaptable to general uses.

The newer Geon 200 series of vinyl chloride, vinylidene chloride copolymers, has been developed to meet the need for polyvinyls which combine increased solubility and thermoplasticity with stability, chemical resistance and wide useful temperature range. In common with the Geon 100 series, these copolymers exhibit

PROPERTIES OF GEON RESINS*

Geon Number	Specific Gravity	Average Acetone Extract	Average Specific Viscosity†	Recommended Per Cent Solids in M.E.K.‡		Weight of Di-octyl Phthalate per 100 Weights Resin to give Comparable Hardness at R.T.
				at 20°C	at 70°C	
101	1.40	15%	0.55	4.5	12	43
102	1.40	14%	0.59	4.5	12	43
202	1.42	48%	0.40	8	17	34
203	1.43	56%	0.36	14	25	31

* Manufactured by B. F. Goodrich Co.
† At 20°C of 0.4% solution in Nitrobenzene.
‡ Methyl Ethyl Ketone.

stability to light and to thermal decomposition. Moreover, in the field of vinyl chloride copolymers, their resistance to hydrolysis by boiling water or even hot alkali is outstanding. Geon 202 is a general purpose copolymer, somewhat more soluble and more thermoplastic than either 101 or 102. Geon 203 has still greater solubility and thermoplasticity.

Geon resins when compounded lend themselves to processing in many ways, including injection and compression molding, extruding, calendering, solution coating, impregnating and film casting.

By proper formulation, they can be modified to produce compositions varying in properties from those of a rigid thermoplastic, through an elastomeric range, to a very soft jelly. Each of the compositions so formed exhibits the essential characteristics of the base resin. These resins combine rubber-like properties with non-flammability and resistance to oxidation. The 100 series Geons are reported to be outstanding in their resistance to deformation at elevated temperatures.

Expected applications include coating of fabrics, paper, foil and other materials; insulation of wire; film for packaging and production of extruded and molded products.

MARVINOL

This is a new vinyl material developed by the Glenn L. Martin Company of Baltimore, aircraft manufacturer.

Extensive commercial tests have shown the value of Marvinol in hospital, household and industrial safety glove applications, where the usual plasticized vinyl materials have not been satisfactory because of plasticizer loss due to emulsification or extraction. For example, surgeons' gloves made from conventional plasticized vinyls shrank and became brittle at the temperatures of steam sterilizations.

Although most work on Marvinol has so far been confined to war applications and those that the existing synthetics have not been able to meet, such as inner tubes and surgeons' gloves, it will probably have many postwar applications.

Complete data regarding Marvinol are not yet available, but the accompanying tabulation shows a few important properties.

PHYSICAL PROPERTIES OF MARVINOL

Tensile strength	2000–1000 psi
Elongation	450%–650%
Tensile strengths for less elastics stocks (200% elongation) may be as high as 3000–4000 psi	
Tear strength	250–175 lb/in.
Standard crescent specimen on Scott machine	
Density	1.20–1.30
May be varied widely by selection of fillers.	
Hardness (room temperature)	60–40
Shore Durometer A Scale	
Densities and hardness values may vary widely by proper selection of fillers.	
Softening point	300°–250°F
Determined by extrapolating curve of hardness vs. temperature to point of zero hardness.	(149°–122°C)
Elasticity (room temperature)	60–85
Shore Elastometer	
Low temperature flexibility	Remains flexible to
Lowest temperature dependent upon composition (−51°C)	−40° to −60° F (−40° to −51°C)
Flex temperature buildup	Very low
Flex life	Very good
Resistance to abrasion	Very good
Dielectric strength	
With 60-cycle alternating potential of 10,000 volts (rms value) a sheet of Marvinol about 0.030 in. thick will show a current leakage of 10 milliamperes or less. This value, which is approximately 1.0 milliampere leakage per thousand volts, is comparable to an exceptionally good grade of rubber.	
Permeability to gases	Exceptionally low

DATA SHEET FOR MARVINOL

Milling

Basic formulation should be mixed on any conventional compounding mill or kneading machine (Banbury) at 200° to 210°F for 5 to 15 min.

Molding

Type of mold	Any conventional positive or flash type compression mold. Also plastics and rubber extruders.
Mold surface	Chromium is preferred; nickel or cadmium are also good. Although iron is not desirable, high-grade steel molds are satisfactory for dark-colored materials.

DATA SHEET FOR MARVINOL—*Continued*

Molding pressure.......	200 psi or less for flash type molds. Any pressure above 200 psi is satisfactory for positive type mold.
Molding temperature.	290° to 295°F (145°C). Slightly higher for extrusion.
Molding time..........	Dependent upon thickness, although a time period of 3 min. has been found satisfactory for thicknesses of 0.080 in.
Mold lubricant.........	Any ordinary soap or wetting agent. (Aquarex D best.)

Notes: Marvinol is a thermoplastic material and requires cooling of the stock to at least 100°F before the mold is opened *or the pressure released.* Extrusions should be allowed to cool before being submitted to strains such as winding on rolls.

VINYL BUTYRAL AND VINYL FORMAL RESINS

Polyvinyl butyral resin has been widely used since 1936 in safety glass as the flexible mid-sheet in the sandwich. Since 1940, it has undergone extensive development and found many new applications particularly as a replacement for rubber.

Compounds of polyvinyl butyral resin appeared early in the war as elastomers for fabric coatings and free film, and in molded and extruded products. Since then their use, primarily in fabric coatings, has expanded widely in such articles as military waterproof clothing, flotation gear and lister bags. The material when available in greater quantity may find important uses as hospital sheeting, baby pants, upholstery coatings, sportswear, free film, etc.

Polyvinyl butyral resin is one of the polyvinyl acetals made by the reaction of aldehydes with polyvinyl alcohol. By varying the degree of plasticization and the quantity and type of fillers and other ingredients, it can be compounded into plastics ranging from hard, stiff molding materials to extremely soft and extensible products. It can be made in a wide range of colors, including clear colorless transparent.

Polyvinyl butyral plastics are unique among the vinyl elastomers in that, by incorporation of certain ingredients, they can be cured in a manner similar to the vulcanization of rubber. Such curing renders the plastic more resistant to heat and insoluble in all common solvents. It also allows the rubber processor to employ the plastic in ordinary operations in virtually the same way as rubber.

Vinyl butyral plastics can be handled on practically all rubber-processing equipment. Unlike many vinyl resins, the butyral can be

calendered at the low temperatures usually used for rubber to produce high-quality films and coatings that are free from defects. It can be extruded on usual rubber tubing machines; can be spread-coated from alcohol solution on either rubber- or pyroxylin-type coating equipment and with certain precautions can be molded in rubber-type molds. It can also be made into soft or hard sponge of low density by any of the standard expanding processes common to the rubber industry.

Polyvinyl formal, the reaction product of formaldehyde and polyvinyl alcohol, can also be compounded into an elastomer many of whose properties are similar to those of the butyral. The formal has the chief advantage over butyral of excellent inherent resistance to hydrocarbons of all types, making it highly suitable for insulation for electrical wires and cables. Experience with the formal, however, has been much more limited than with the butyral.

PROPERTIES. Vinyl butyrals can be made to give coatings or free film of extraordinary softness, flexibility and attractive texture — factors which when coupled with the inherent colorless transparency of the basic material make possible the preparation of articles that are pleasing in appearance and feel. Color possibilities are said to be unlimited.

Unlike resins containing chlorine, vinyl butyral ages well and, when properly compounded, does not discolor in light over a long period of time and has excellent resistance to oxidation. There is no reported case of deterioration of fabric caused by butyrals.

Vinyl butyrals have tensile strengths varying from 1000 lb. per sq. in. for the very soft stocks to 3500 lb. per sq. in. for the tougher molding types. Corresponding elongations at break are 400 and 200 per cent. Water absorption varies from 3 to 5 per cent. Water permeation is quite low, but the permeation of water vapor is relatively high compared with such materials as vinylidene chloride. Resistance to salt water and acids is better than resistance to pure water, but acids will darken the color. Strong alkalies are not recommended for prolonged exposure but have no injurious effect over short periods.

Soaps and common washing chemicals have no harmful effects other than slight extraction of plasticizer by hot water, resulting in some stiffening after many washings. Cured stocks can be washed in hot water, boiled, or steam sterilized with no effect other than slight plasticizer extraction. Thermoplastic film cannot be washed in any more rigid conditions than warm water and soap and should be dusted with talcum powder after washing.

Abrasion resistance of vinyl butyrals is excellent. Permanent set in most fabric coatings stocks is high, but special compounding will give fairly low permanent set at temperatures as high as 160°F. Flex fatigue strength is very poor, particularly if the material is flexed rapidly, and vinyl butyral is not recommended for applications requiring this property.

Vinyl butyrals show a resistivity to temperature change equal to that of most vinyl resins. The material stiffens with reduced temperature, but few stocks would have a brittle temperature above −40°F. and some are below −90°F. Applications requiring high elongation at very low temperatures are not recommended, however. At elevated temperatures thermoplastics are not to be used above about 130°F. as free plastic and about 160°F. as coatings. Cured stocks begin to lose strength at about 140°F., but black stocks have been made with considerable strength at 200°F. Cured coatings are limited in temperature only by plasticizer volatility, which will allow use for several days at 200°F. with little effect and short exposure to 300°F.

Some vinyl butyrals as a thermoplastic are soluble in all lower alcohols, but other resins are not soluble in methyl alcohol. Ethyl alcohol is the standard solvent and can be diluted with naphtha, aromatics, ketones or esters. Cured stocks swell in alcohol but are not soluble, a good test for completeness of cure. Other solvents such as hydrocarbon oils, aromatics, esters and ketones attack the plastic only through extraction or plasticizer, resistance to oils being quite good.

Vinyl butyral is not to be compared with rubber as a rubber "substitute." It is a "dead" material, and when distorted its recovery is slow. It sometimes gives a deceptive feel of weakness because

its initial distortion as a free film or sheet is relatively easy. This low modulus distinguishes butyral from other vinyl resins and allows extreme softness of texture without sacrifice of ultimate strength.

Applications. Following are listed some military applications using large quantities of vinyl butyral and also suggested uses in civilian work.

Military uses, for which polyvinyl butyral has been on direct government allocation:

Single-coated fabrics for Army raincoats, ponchos, food bags, clothing bags, flotation gear, vesicant-gasproof fabrics.

Heavy-coated duck for Army and Marine Corps water bags, pontoons, and other flotation gear.

Double-textured coated fabrics for Marine Corps ponchos, Navy and Marine Corps raincoats and Navy stormsuits.

Experimental uses such as heavy-duty hose, film for liquid waterproof packaging, miscellaneous molded parts for Army trucks, coated fabric for scabbards.

Civilian uses, some of which have received some resin allocation through the war and some of which are proposed for postwar applications of particular interest:

Coated fabrics for such uses as baby pants, crib sheeting, hospital sheeting, waterproof clothing of all types of rainwear, sportswear, children's wear, waterproof table cloths, drapery and upholstery, shower curtains, waterproof containers for handbags and cosmetic kits, waterproof webbing, baby bath-tubs, mattress covers.

Free film for sundries such as baby pants, crib sheeting, surgical goods, make-up capes, tobacco pouches, liquid waterproof covers and containers, shower curtains and many similar applications.

Heavy sheets and coatings for luggage, handbags and similar applications.

Extruded tubing for uses where transparency and chemical resistance are important as in medical tubing.

Molded goods and sponge for vibration damping and chemically resistant applications.

PHYSICAL PROPERTIES OF TYPICAL THERMOSETTING VINYL BUTYRAL COMPOUND

Tensile strength, psi	1,470
% Elongation (ASTM Method D-412)	300
Tear strength, psi (ASTM Method D-624)	120
Permanent set, % (ASTM Method D-395 — constant deflection)	
25°C	27
71°C	25
Brittle temperature, °C (ASTM Method D-746)	−40
Modulus of elasticity in flexure, psi (ASTM Method D-747)	
+25°C	About 200
−35°C	68,000
−57°C	222,300
Water absorption, % 24 hr at 25°C (ASTM Method D-570)	2.2
Plasticizer loss after water absorption test, %	0.2
Plasticizer loss after heating 72 hr at 82°C, %	1.6
Abrasion resistance, du Pont abrader, cc/hr/hr	107

Chemical resistance — 7 days immersion at 25°C

3% sodium chloride solution	— 2.1% absorption	— no effect
10% sodium hydroxide solution	— 7.4% absorption	— color darkened
30% sulfuric acid solution	— 3.4% absorption	— color darkened
100 octane gasoline	— 9.2% absorption	— slight stiffening after drying
Toluene	— 67% absorption	— bad softening

CEREX

Monsanto Chemical Company has developed a new heat-resistant thermoplastic injection-molding material, Cerex. This is a styrene copolymer having an A.S.T.M. heat distortion point of 212° to 230°F., which compares with 168° to 176°F. for polystyrene.

This high heat resistance should make it useful to injection molders, who have been limited heretofore to materials with distortion temperatures below 200°F. Parts molded of Cerex to close dimensional tolerances retain their dimensions and mechanical strength during prolonged exposure at temperatures over the boiling point of water, according to Monsanto engineers. Molded parts may be sterilized in boiling water or used at ambient temperatures in a range hitherto restricted to thermosetting plastics.

The increased heat resistance of Cerex has been obtained without sacrificing molding qualities. The material may be injection molded on standard machines in molds designed for other thermoplastics.

TENTATIVE DATA SHEET

CEREX

	Cerex	Polystyrene
Injection molding temperature:		
Cylinder	370°–450°F	400°–450°F
Mold	170°–250°F	150°F
Specific gravity	1.07	1.05–1.07
Flexural strength, psi	13,000	8,000–10,000
Impact strengths:		
Charpy — notched	0.46 ft-lb in.	0.30–0.37 ft-lb/in.
Izod — notched	0.40 ft-lb/in.	0.30–0.40 ft-lb/in.
Izod — unnotched	3.48 ft-lb/in.	2.64 ft-lb/in.
Distortion temperature standard	212°–230°F	168°–176°F
Rockwell hardness	M-100	M80–M90
Dielectric strength	510 v/mil	500–700 v/mil
Dielectric constant:		
60 cycles		2.5–2.6
1000 cycles	2.72	2.5–2.6
1 megacycle	2.76	2.5–2.6
Power factor:		
60 cycles		0.0001–0.0003
1000 cycles	0.0024	0.0001–0.0003
1 megacycle	0.0024	0.0001–0.0003
Arc resistance	69 sec	61 sec
Burning rate	Slow	Slow
Water absorption, ASTM 24 hr	0.30%	0.05%
Effect of:		
Weak acids	None	None
Strong acids	Oxidizing acids attack	Oxidizing acids attack
Weak bases	None	None
Solubility	Soluble in aromatic and chlorinated hydrocarbons	Soluble in aromatic and chlorinated hydrocarbons
Clarity	Amber transparent	Transparent
Color possibilities	Extensive	Unlimited

The mechanical strength of Cerex is comparable with Lustron (Monsanto polystyrene), although data taken on specimens prepared from pilot-plant production indicate somewhat higher impact and flexural values.

Cerex retains the excellent acid and alkali resistance of the

polystyrene and is resistant to carbon tetrachloride and aliphatic hydrocarbons.

The electrical loss properties of the new material at high frequencies are good, although not comparable with the polystyrene. In many applications where extremely low loss properties are desirable, thermal demands necessitate the use of mica-filled phenolics as a compromise. Where good strengths are not needed, Cerex materials meet many such service temperature requirements and are suitable to replace mica-filled phenolics by reason of improved insulating performance and adaptability to injection molding.

Among the projected uses of the new material are surgical instruments, electronic instrument parts, sterilizable combs and plumbing hardware. Cerex may be considered for any application where injection molding is desirable, but where standard thermoplastics are unsuitable because of the low heat resistance of the moldings.

Cerex will probably sell in the upper bracket of the price range of the established thermoplastics.

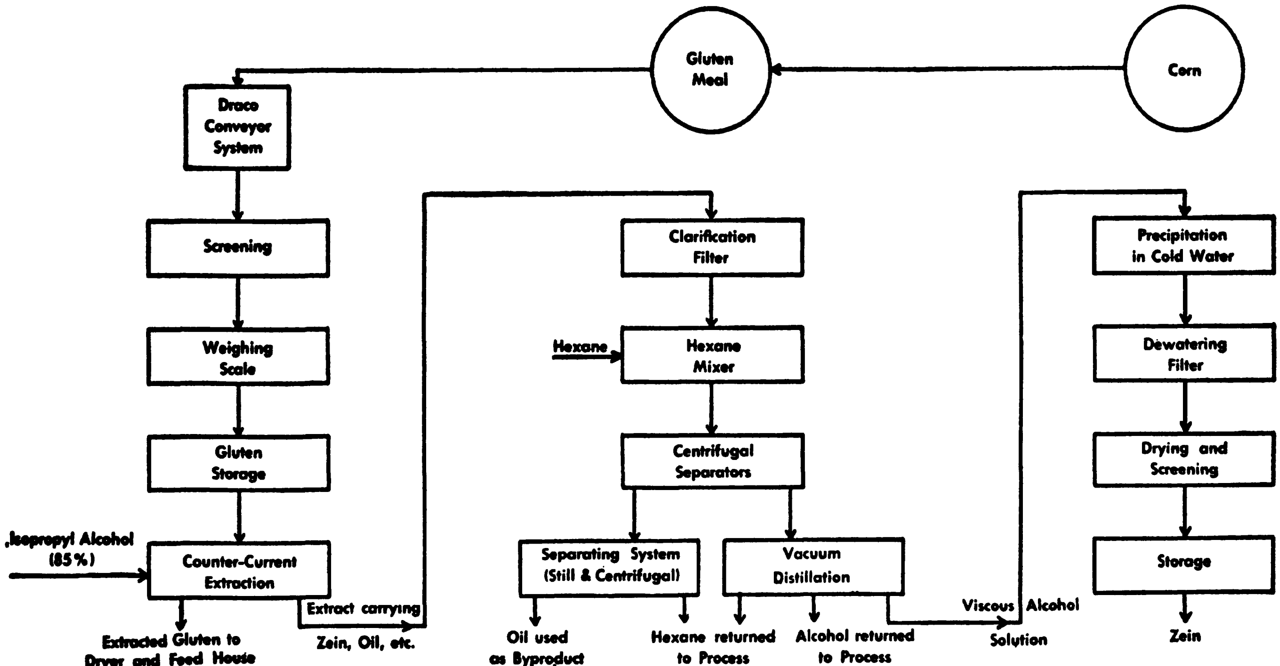
The natural color of Cerex resin is a light amber, but a wide range of transparent, translucent and opaque colors can be obtained by incorporation of dies and pigments.

ZEIN

Zein, a protein derived from corn gluten, was developed by Corn Products Refining Company many years before the war but did not come into much prominence until after Pearl Harbor when the supply of natural shellac from India was cut off. Since then, demand for zein has increased markedly.

A chemist named Gorham isolated zein in corn in 1821 and named it after Zea, the scientific name of the corn family. Zein is the only commercially available protein soluble in alcohol, but it remained a laboratory curiosity for 70 years, principally because no process was available for extracting it in quantity.

In 1891, Prof. Thomas B. Osborne of Yale University formulated and patented a new composition utilizing zein as its principal ingredient for use as a varnish, lacquer or glue. But he failed to work out a process for the commercial extraction of zein and his patent lapsed, virtually forgotten.



Courtesy Chemical Industries

FIG. 13. Simplified flow sheet for extraction of zein from corn at Corn Products Refining Co. plant, Pekin, Illinois.

During the depression, the Corn Products Refining Company, in a search for additional products that could be extracted from corn along with starch, oil, dextrose and others, found a practical method for the extraction of zein.

Before the war, zein was used principally as an ingredient for compounds for the protective and decorative coating of paper, but it has a wide range of possible applications and its development was greatly accelerated by the war. The War Production Board put it under allocation in May, 1943, and Corn Products Refining Company, which was the only supplier, stepped up production to sizable commercial quantities. Zein is used as a basic ingredient of greaseproof, heat-sealing paper coatings for military packages, as a substitute for shellac and as a core wash for magnesium foundry castings. Its outstanding quality is resistance to various hydrocarbons such as oils, greases, turpentine, benzine and similar solvents. It is so completely insoluble in the hydrocarbons that it can be boiled in oil, turpentine, benzine and similar solvents without undergoing a change. It is compatible with fatty acids of the amine and amide types and blends readily with synthetic plastics of the phenolic, melamine and glyptal types.

It has been blended with rosin in various proportions by the Filtered Rosin Products Company of Brunswick, Georgia, and one of these combinations is known as Chemlac, a substitute for shellac.

Zein's potentialities as a replacement for rubber have also been the subject of much study. A heavy solution of the protein and any one of several plasticizers can be blended with fillers and curing agents and worked on standard rubber-making machinery to make a rubber-like material. This material has a tensile strength of 1200 lb. per sq. in. and an elongation of 250 per cent. Tensile strengths up to 2000 lb. per sq. in. can be achieved by sacrificing elongation.

While such properties are far below the 4200 lb. per sq. in. tensile strength and 500 per cent elongation of high-grade natural rubber tread stock, the material can be molded and "vulcanized" (with one of the aldehydes taking the place of sulfur as a curing agent) into a wide variety of oil-resistant, abrasion-resistant "rubber goods."

Some of the possible applications under investigation are long-

wearing zein shoe soles and heels that will not slip on wet surfaces, zein shoe cements to replace those based on natural latex, raincoat coatings in a wide range of colors, stair treads and floor mats, sink mats and stoppers, gaskets for jar closures and printing type for rubber stamps.

Potential uses include molding powder, coating adhesives and laminates, and films and fibers. The latter forms suggest possible postwar uses of zein in the packaging as well as the textile field.

More than 250,000,000 lb. of zein are theoretically available from the 100,000,000 bu. of corn ground and processed annually in this country for starch, sugar and other products. It has been practical, however, to get only about 1 lb. of zein out of every 56-lb. bushel of ground corn. Considerable research on zein is under way by Corn Products Refining Company, which foresees important postwar uses of this material.

ZINLAC — WARTIME SUBSTITUTE FOR SHELLAC

For a number of years before the war, William Zinsser and Company, the leading importers of shellac, employed Arthur D. Little, Inc., on research problems. As war in the Pacific became imminent, their work was concentrated on development of a substitute for shellac. The result was Zinlac, a varnish that can be handled like shellac, equals it in most properties and surpasses it in some.

An important ingredient of Zinlac is zein. In the development of a shellac replacement utilizing zein, it was found that the final product had a tendency to set to an irreversible gel in shipping containers, but further research developed a method (patent applied for) that overcame this difficulty.

Natural shellac possesses a remarkable combination of properties including unusual hardness, toughness and adhesion, sufficient flexibility to give a good film, good electrical properties and easy solubility in alcohols and alkalies. Solutions in alcohol have a comparatively low viscosity, so that fairly concentrated solutions can easily be prepared, and the resin film gives up its solvent rapidly in drying. Shellac carries a small percentage of natural wax which gives opacity to the alcoholic solution because of its insolubility,

but the dried film is transparent because the wax and resin constituents have approximately the same refractive index. The wax content is important as a natural plasticizer in increasing the fluidity and wetting power toward fillers when the shellac is fused and in increasing the water resistance. Certain uses of shellac are dependent on the fact that a film is sufficiently porous to permit the passage of water vapor and other volatile materials and yet seals in liquids that are not soluble in it. The coloring matter in orange shellac can be removed by bleaching to give a light-colored product that is virtually colorless as a film. Shellac was generally available before the war at fairly reasonable prices.

Zinlac is in many ways similar to shellac varnish. Because denatured alcohol is used as the solvent, no penetrating or objectionable odors are involved in its application. Like shellac varnish, it can be readily thinned to any desired concentration. The varnish dries rapidly — slightly faster than shellac varnish of an equal concentration.

Like shellac, Zinlac is made in "white" and "orange," though it resembles a dewaxed or refined shellac solution (French polish) rather than the opaque ordinary shellac. It can be applied by brushing or by spraying, and it bonds well to wood or metal.

The Zinlac film is unusually hard and tough. Sanding is slightly more difficult than with shellac or other sealers. When applied to wood, its properties are midway between those of shellac and lacquer. Shellac penetrates farther, and a very thin coat will soak virtually all the way into the wood, particularly if the wood is open grain. Lacquer has a tendency to lie on top of the wood. Zinlac possesses some of the advantages of each. It anchors well but does not penetrate to the extent that shellac does. It is excellent as a building coat under varnish.

Zinlac has outstanding qualities as a label varnish. It has been widely used as a priming coat on metal for military tanks and ships previous to painting. The Zinlac film is less permeable to moisture than a shellac film, and it does not whiten in contact with water as much as shellac does. Its electrical properties are unusually good. White Zinlac meets the new Federal Specifications for Shellac

Varnish Replacement. Briefly, these may be summarized as follows:

1. *Appearance.* Free from sediment, suspended matter and without clotting or gelatinization.
2. *Color.* No darker than a solution of 1.041 g. of potassium dichromate in 100 ml. of pure sulfuric acid, sp. gr. 1.84.
3. *Viscosity.* Not less than 0.0624 and not more than 1.65 poises.
4. *Nonvolatile Matter.* Not less than 30 per cent by weight.
5. *Ash.* Not more than 1.0 per cent based on nonvolatile content.
6. *Drying Properties.* Shall set to touch in not less than 1 min., or more than 10 min., and dry hard in not more than 3 hr.
7. *Working Properties.* Shall have satisfactory brushing and leveling properties.
8. *Adhesion Properties.* Shall adhere satisfactorily to both metal and wood.
9. *Effect on Wood.* Shall not raise the grain or discolor wood to a greater extent than a similar cut of orange shellac.
10. *Resistance to Abrasion.* Must pass sand abrasion test as outlined.
11. *Odor.* Must not be abnormally offensive or disagreeable before, during, or after drying.
12. *Dilution.* Must stand specified dilution test without precipitation, separation or cloudiness.
13. *Sanding Properties and Sealing Properties.* Must be at least equal to shellac in specified tests.

In a comprehensive series of tests of Zinlac and the best grade of 5-lb. white shellac, the independent laboratory of Barsky and Strauss came to the following conclusion:

> As compared with pure white shellac under the conditions of these tests, white Zinlac showed equal spraying and leveling qualities, more rapid dry and greater resistance to sanding and rubbing. The sanding and rubbing qualities of Zinlac resembled those of lacquer.
>
> On comparing the rubbed surfaces of three-coat work, Zinlac was equal to shellac in fullness, filling qualities, color and smoothness. The Zinlac finish was definitely harder than the shellac, in both surface hardness and through hardness.
>
> The laboratory tests on recently finished panels indicated that Zinlac was definitely better than shellac in print resistance, moisture resistance and hot dish resistance; equal to or slightly superior to shellac in bump resistance, mar resistance and scratch resistance.

The applications of Zinlac have been numerous, and it has been used as a surface coating in the following military applications:

Aircraft manufacture	Machine tools
Airfield construction	Munitions
Armament	Naval construction
Caskets	Overseas boxes
Communications	Patterns
Furniture	Radio and electronics
Gas masks	Refrigerators
Gliders	Shipbuilding
Jigs	Skis and snowshoes
Life rafts	Tanks, armored
Machinery	Vehicles

It has been used on war essential uses in these additional lines:

Bobbins and shuttles	Pharmaceuticals
Federal housing	Polishing wheels
Food machinery	Railroads
Handles for tools	Telephone-telegraph
Paper for food	Veterans hospitals

The future of Zinlac will depend on many factors, particularly its price as compared with white shellac varnish. During the war Zinlac has sold and may continue to sell after the war for considerably less than white shellac varnish. If the difference is great, the advantages will be heavily in favor of Zinlac. If these materials approach each other in price, each will stand on its own merits and reputation, and Zinlac may cut into the shellac market somewhat.

Zinlac has some outstanding characteristics that should make it a most useful addition to the field of protective coatings. It is superior to most "shellac substitutes" previously available and if it did nothing more than take their place, its future might be assured. With the war limitation on shellac and limited imports, use of Zinlac received a great stimulus.

In the past, shellac retained its popularity and usefulness, even though various substitutes appeared on the market, largely because

extensive research to improve its quality and develop new uses has been carried out in this country, in India and in Great Britain. When it becomes available again, however, it will have a more formidable competitor.

ANOTHER SUBSTITUTE FOR SHELLAC

Westinghouse Electric and Manufacturing Co. has recently announced a new shellac substitute which, it is anticipated, will prove of considerable importance in the electrical industry.

At the beginning of the war, we were faced with the prospect of losing our shellac supply since all of it comes from India. Moreover, made by small insects from the saps of several kinds of trees and varying in quality with the seasons, natural shellac is an extreme example of a product full of impurities. Yet one highly important and troublesome electrical device — the commutator of rotating machines — has depended almost completely on shellac as a bonding insulating agent.

While shellac had given much trouble, previous research had provided no satisfactory substitute. The war, however, stimulated further research and chemists again took the shellac molecule apart theoretically and postulated another hypotheses as to the type of the desired resin. The result was a strong, new synthetic resin.

Mechanically and electrically, this resin appears to have all the properties desired; indeed, it may be an improvement over shellac at its best for commutators and in certain other electrical insulations. It promises to eliminate not only shellac but also its associate, mica (used in combination with shellac in commutators).

Fiberglas bonded with this resin has a tensile and bending strength equal to that of rather strong metals — 75,000 to 80,000 lb. per sq. in. In other words, this plastic is stronger than cast iron which has a tensile strength of 15,000 to 50,000 lb. per sq. in., stronger than sheet brass with a tensile strength of 40,000 to 70,000 lb. per sq. in., and as strong as many steels (tensile strength: 80,000 to 300,000 lb. per sq. in).

BAGASSE

A practical commercial molding compound was developed in 1941 from bagasse, the lignocellulosic residue of cane-sugar manufacture, as part of a program to utilize agricultural waste. Bagasse was already familiar in the form of wallboard made by Celotex Corporation, which had obtained considerable publicity as a result of its application in the building industry. The newest development, however, is the use of bagasse in molding compounds.

The molding industry is now using the new compounds satisfactorily, and a growing demand has made it necessary to expand manufacturing facilities from the original pilot-plant scale into a full-sized commercial unit. Research has been directed toward the development of two products — a general-purpose and a semi-impact molding compound — and improvements in the physical and molding characteristics of these compounds. They both mold well and have excellent preforming characteristics and rapid curing cycles.

A new thermoplastic resin based upon bagasse has been developed in the effort to find a molding compound that could be manufactured without any critical raw materials. Its properties make it a possible substitute for shellac in the manufacture of phonograph records, and commercial production started in September, 1942.

A series of bagasse resins with considerably different chemical compositions but with only slightly different physical characteristics has been developed. These resins are dark brown in color, hard and somewhat brittle, and they have softening points that vary between 185° and 220°F. according to the formulation. Several have proved satisfactory for record manufacture. A product that uses chemicals which have been under restriction is reported to be superior to those now being manufactured and capable of substituting completely for shellac in record manufacture. These resins are made in either lump or flaked form and packed for shipment in 100-lb. multiwall paper or used burlap bags. They may be used even after shellac again becomes plentiful.

A water-soluble thermosetting bonding resin made from the alcohol-soluble resin, suitable for use with paper, cloth and veneers, has been developed. Its outstanding characteristics are extreme

solubility in water, rapid cure and relatively low temperatures and pressures required for complete curing. Good bonds have been obtained with canvas and cotton drill at temperatures of 270°F. and pressures as low as 75 lb. per sq. in. After curing, the resin has an unusual degree of flexibility and becomes very resistant to water.

The Valite Division of Valentine Sugars has pioneered in the development of plastics from bagasse and markets all its products under the trade name Valite. These include: (1) a series of thermoplastic resins that have been used in large quantities in the past few years as an extender or substitute for shellac in phonograph records; (2) a general-purpose thermosetting molding compound composed of a resin derived from bagasse and a bagasse filler;

TABLE I. PHYSICAL PROPERTIES AND CHARACTERISTICS OF 4 TYPICAL BAGASSE PLASTIC COMPOUNDS[1]

Compound	A	B	C	D
Molding quality	Excellent	Excellent	Good	Good
Molding temperature, °F	300-350	300-350	300-375	300-375
Molding pressure, psi	2000-3000	2000-3000	2000-10,000	2000-10,000
Compression ratio	2.5	2.5	3.0	3.0
Specific gravity	1.35-1.40	1.35-1.40	1.30-1.40	1.30-1.45
Flexural strength, psi	8900	9500	10,160	9500
Impact strength, unnotched Izod, ft-lb, ½-in. × ½-in. bar	1.10	1.00	1.39	1.25
Resistance to heat, °F	350	380	400	400
Dielectric strength, v/mil, step	250	[2]	[2]	[2]
Water absorption 48 hr, %	0.90	0.75	[2]	[2]
Burning rate	Very low	Very low	Very low	Very low
Effect of age	Apparently none			
Effect of weak acids	Slight			
Effect of alkalies	Slight surface roughening, 168 hr boiling with 25% sodium hydroxide			
Effect of organic solvents	None, to a slight surface roughening			
Effect on metal	Inert	Inert	Inert	Inert
Colors	Dark	Dark	Dark	Dark

[1] Owing to the limited amount of commercial experience, with these materials, only laboratory results are available. Data given above should be considered as indicative of the properties of these materials and not taken as a guarantee of performance.

[2] No data available.

(3) a semi-high-impact molding compound composed of the same resin and another type of filler (also made from bagasse); (4) a thermosetting water-soluble laminating resin, derived from bagasse, which can be used at low temperatures and pressures such as are employed in bag molding, or equally well at the high temperatures and pressures normally used for sheet stock.

The company reports that its work on molding compounds and laminating resin has been somewhat handicapped by wartime restrictions, but that progress has been made in recent months and a growing use of the materials is anticipated.

PLASTICS FROM REDWOOD

Within the past few years the giant redwood tree, which grows near the Pacific coast, has been utilized for making plastics. The Pacific Lumber Company of Scotia, California, instituted a long-term research project at The Institute of Paper Chemistry in order to reduce the amount of redwood going to waste in lumber operations.

The redwood tree is notably resistant to rot. Some have lain hundreds of years in the muck of the forest, with ferns and even full-grown redwoods over their half-buried trunks, only to take their place on the production lines leading to the head-rig and trimmer saws. The principal constituents of the wood substance of redwood are much the same as those of other trees, namely, cellulose, lignin and the large group of carbohydrates known as the hemicelluloses, including both pentosans and hexosans. The remainder consists of materials soluble in water and organic solvents, which give redwood such characteristic properties as longevity and resistance to mold and bacterial attack.

Redwood in the form of wood flour comes close to being a thermoplastic. It may be molded directly, without any added material, to give a product that looks like an article molded from a conventional molding powder. Because of poor flow characteristics and lack of adequate water resistance, molding redwood flour alone is not a commercial operation. Low flow means high pressure for molding; in this case about 5000 lb. per sq. in. and 320°F. being

required to produce a simple disk. The degree of flow and nature of the product are related to the extractive content. The sapwood cannot be made into a molded article of any practical importance. Roots, however, give a somewhat more interesting product. Redwood flour can be improved in its molding characteristics by adding agents, or plasticizers, which improve flow, such as glycerin in which the plasticizer is present to the extent of 10 per cent. An additional improvement is obtained when a hardener such as hexamethylenetetramine is added. It is then possible to mold an article that is strong and fairly serviceable. For example, test pieces have been molded, having the following characteristics:

Impact, Charpy unnotched	1.03
Tensile, psi	6,450
Flexural, psi	10,433

They were made from a molding powder of the following composition:

Redwood flour	91.5%
Glycerin	3%
Hexa	5%
Condensation black	0.5%

The parts were molded at 4000 to 5000 lb. per sq. in. and 320°F. The principal disadvantage is the great pressure required for molding.

Redwood flour has a second use in plastics as an extender for phenol-formaldehyde resins. However, this use is not particularly satisfactory since the products lack sufficient water resistance.

A molding powder of this type has been made from redwood flour and a phenolic resin according to the following formulation:

Stumpwood flour	74%
Durez 114*	25%
Calcium stearate	0.5%
Carbon black	0.5%

These ingredients are mixed for 90 min., milled for 1¼ min. at 210° to 240°F., and then ground. The molding powder should be preheated for 2 min. at 212°F. After curing at 302°F. for 2 hr., this product will give better impact and water resistance.

* Phenol formaldehyde.

The material may be molded at 4000 lb. per sq. in. and 310°F. for 5 min. It is thermosetting and can be used in phenolic molds. Its strength values are as follows:

	Redwood Phenolic (Palco 198)	*Bakelite 3200*
Impact	0.55–0.6	0.610
Tensile, psi	5300	6520
Flexural, psi	7500	8560
Water pickup, per cent in 24 hr	2.5	0.47
Molded density	1.37	1.356

Another method of utilizing redwood wastes for plastics is based upon the discovery that, when they are cooked with steam at high pressure, the tannins and phlobaphenes are modified and combined with modified wood substance to yield a pulp that is superior to redwood flour. The pulp can be molded alone and has the following physical characteristics, when molded at 4000 lb. per sq. in. and 300°F.:

Impact, Charpy unnotched	0.58
Tensile, psi	5480
Flexural, psi	7700
Water pickup, per cent	2.5 to 3

It has several disadvantages when used alone. For example, it is partly thermoplastic, and for ejection the molds must be cooled from 300°F., the molding temperature, to approximately 250°F. Furthermore, the product swells and becomes sticky when exposed at high humidities because of the presence of resins that are still somewhat water-soluble. Nevertheless, alone or mixed with a small amount of lignin or Vinsol, a product can be obtained that has good flow and finish and moderately satisfactory physical characteristics. The strength of a Vinsol modified redwood molding composition is as follows:

Impact, Charpy unnotched (½ × ½-in. piece)	0.45
Tensile, psi	6700
Flexural, psi	8000
Water pickup, per cent in 24 hr (ASTM)	2 to 2.3

Many articles have been molded from a formulation of 95 redwood, 5 Vinsol which has had the advantages of being cheap and available in large tonnage without the use of any critical materials.

Nevertheless, the thermoplastic characteristics of redwood pulp would tend to limit its applications to emergency uses.

A third phase of redwood research has been the development of thermosetting molding formulations. The thermosetting molding powder achieved is the result of a series of chemical reactions. The first involved the conversion of the tannins and phlobaphenes in the redwood to a resinous composition with the normal wood chemicals, as a result of a cooking operation. These constituents could then be further condensed up to the stage of thermosetting materials with a resinous material developed at The Institute of Paper Chemistry. This resinous material is the result of a polymerization of a by-product condensed in turn with formaldehyde. The resin and the redwood plastic pulp are then condensed together by milling in the presence of a catalyst to the point at which they will polymerize in the mold to yield the finished product under manufacturing conditions. The product has the following physical characteristics:

Impact, Charpy unnotched (½ × ½-in. piece)	0.37
Tensile, psi	5000
Flexural, psi	6500
Water pickup, per cent	1

The strengths are not quite so high as those for the straight pulp, but the increase in resistance to water (and incidentally to acids) makes the material much more useful for commercial purposes. Because it is converted to a thermosetting product, the material can be molded in conventional phenolic molds.

Research on redwood by the Pacific Lumber Company is still under way. The most important practical result so far is the utilization of redwood for steering wheels for tractors and trucks ever since the war cut off the supply of rubber and limited the supply of other plastics. A plant constructed at Scotia, California, has a productive capacity of around 2,000,000 lb. of redwood pulp a month.

NOREPLAST

This is the name given to a family of plastics molding compounds developed by the Northern Regional Research Laboratory

at Peoria, Illinois, and utilizing agricultural residues such as straws, stalks, cobs and shells.

Considerable experimentation has been conducted to substitute such materials for wood flour in phenol-formaldehyde molding compounds, but these have generally been regarded as inferior to wood flour. It is claimed, however, that this is because agricultural residues react differently with different phenol-formaldehyde

PROPERTIES OF CERTAIN NOREPLAST MOLDING COMPOUNDS

Compound number	649	650	696	689	General-Purpose Specifications
Composition	Corncob	Corncob	Hemp hurd	Corncob	
% Agricultural residue flour, 80 mesh	50	62.3	62.3	62.3	
% Phenol-formaldehyde resin	47.2A	35.0A	25.0A	35.0B	
% Oleo-resinous plasticizer	None	None	10.0	None	
% Dye, lubricant, and catalyst	2.8	2.7	2.7	2.7	
Flexural strength, psi	11,990	10,040	9100	7500	9000
Tensile strength, psi	10,240	10,210	7450	6180	7000
Izod impact strength, ft-lb-in./in. of notch	0.20	0.24	0.21	0.24	0.24
Unnotched impact, ft-lb, ½ × ½ in. bar	0.88	1.00	0.62	0.51	
Water absorption, ASTM					
% Gain in weight					0.80
½ min molding at 320°F	0.64	2.06	1.19	2.94	
1 min molding at 320°F	0.58	1.43	0.60	1.51	
2 min molding at 320°F	0.48	1.08	0.47	1.32	
2½ min molding at 320°F	0.49	1.04	0.51		
5 min molding at 320°F	0.52	0.91	0.56	1.36	
% Volatile for					
½ min molding at 320°F	0.19	1.28	0.15	0.71	
1 min molding at 320°F	0.29	0.85	0.18	0.74	
2 min molding at 320°F	0.30	0.60	0.49	0.67	
2½ min molding at 320°F	0.32	0.52	0.55		
5 min molding at 320°F	0.37	0.55	0.55	0.63	
Mold shrinkage, in./in.	0.012	0.016	0.010	0.020	0.006 to 0.008
Expansion after 24 hr immersion, in./in.	0.0007	0.0009	0.0006	0.0011	

resins and it is not surprising that inferior results have been obtained when substituting for wood flour in compounds which have been developed specifically for combination with it. By using different proportions of phenol-formaldehyde and corncob residue flour, some interesting materials have been developed. Properties of some of these materials are shown in the accompanying tabulation.

PLASTICS FROM COFFEE

The Brazilian government has in the last few years sponsored considerable research in the utilization of coffee in making plastics. Latest reports indicate that results have been disappointing. The work has reached the pilot-plant stage, but commercial production has not been inaugurated and the war has served to divert attention from such a project.

Technical difficulties have been responsible for the lack of progress.[1] Resins produced from coffee lack sufficient aldehydes, a deficiency that might make large-scale manufacture uneconomical. Research, however, is continuing. The Caffelite Corporation has been identified with this work.

[1] *The Spice Mill*, March, 1944.

CHAPTER IV

Improvements in Materials

VINYLITE ELASTIC MOLDING MATERIALS

The elastic, rubbery type of vinyl plastics are produced from the same type of vinyl resin as the rigid compounds, but, unlike the latter, they contain relatively large amounts of a plasticizer or softening agent, which accounts for their rubbery nature. With the shortage of rubber, interest in these materials has increased greatly, and they are now being employed for hundreds of direct rubber replacements. These vinyl elastomers are adaptable to both injection- and compression-molding processes.

Vinyl elastic molding materials are immune to most of the factors that cause natural rubber to deteriorate, since they are highly resistant to water and oil, and do not oxidize upon aging. Their tensile strength is greater than that of rubber compounds of comparable hardness. They are more than three times as resistant to abrasion, and they have an exceptionally long flexing life. However, these elastomers have a slower rate of snapback, and a lower safe operating temperature than rubber. In addition, the fact that they may be produced transparent and in an unlimited range of colors offers styling possibilities for postwar products. Advantages also exist over natural rubber in fabricating methods. Since they are thermoplastic, these elastomers do not need to be vulcanized, and, unlike rubber, they may be molded by the economical injection-molding process.

Large-scale use of vinyl elastic plastics for molding has occurred only recently. Already, however, compounds in a wide range of hardnesses are being produced for a number of electrical and mechanical applications such as transparent wire terminal insulator sleeves, "mole" insulators, grommets, bumpers, and many others.

PROPERTIES OF TYPICAL VINYLITE ELASTOMERS

	Type 30	Type 35	Type 40	Test Method (ASTM Test No.)
Tensile strength, psi	2500	2000	1300	D-412-41
Ultimate elongation, %	300	330	350	D-412-41
Olsen stiffness index, $\times 10^{-4}$ in.-lb (0.040 in. spec.)....	145	96	56	
Low temperature, flexibility, TF, °C................	—17	—30	—39	
Tear resistance, lb/in.......	30	25	20	D-532-39T
Hardness, Durometer "A"..	86	75	67	
Fatigue resistance, cycles to failure................	500,000	>1,000,000	>1,000,000	
Abrasion loss, volume in proportion to "B" rubber as 100..................	80	70	62	
Flammability, burning rate, sq in./sec, 0.040 in. thick..	Nonflammable			D-568-41T
0.020 in. thick	0.2	0.3	0.4	
Specific gravity...........	1.23	1.20	1.18	D-71-27
Specific heat between 18 and 38°C (cal) $(gm)^{-1}(°C)^{-1}$..	0.33	0.35	0.36	

Resistance to water, oils and chemical reagents:

These formulations are very resistant to water, soapy water, dilute acids and dilute alkalies, but stiffen when immersed in alcohol, gasoline and oil. Other compositions have improved resistance to alcohol, gasoline and oil.

IMPROVEMENTS IN METHYL METHACRYLATE

The most important recent improvement in methyl methacrylate has been the development of molding powder capable of yielding molded articles that are considerably more resistant to heat than any of the types previously available.

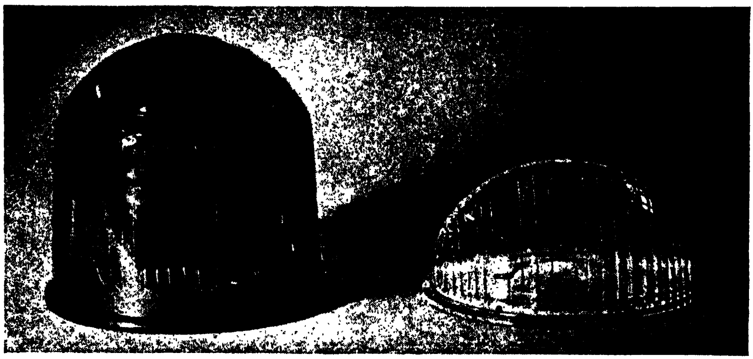
The new powder will withstand service temperatures 30° to 40°F. higher than the service temperatures of articles molded from the conventional types, or from 160° to 180°F.

E. I. du Pont de Nemours & Company, Inc., in announcing this special formulation, points out that it is a wartime development, but will be available for numerous peacetime uses.

Many articles molded from this new powder will not soften

appreciably or distort when exposed to a temperature of 212°F., the boiling point of water.

The new material has approximately the same mechanical, optical, electrical and molding properties as the general-purpose Lucite molding powders now used for reflectors on military vehicles, Army compasses, Navy control equipment, indicators and other items of ordnance. Articles may be crystal clear, or the powder may be dyed or pigmented to desired colors.



Courtesy E. I. du Pont de Nemours & Co., Inc.

Fig. 14. Old airfield light lens at left weighed 39 ounces. New Lucite lens at right, which fills same function, weighs 3 ounces.

The new powder was developed for use in existing compression, injection and extrusion equipment. The best technique for molding this powder requires injection temperatures 30° to 50°F. higher than are used for conventional Lucite. It is advisable, however, to employ the lowest temperature at which the die cavities will fill.

Available in granular form for compression molding, the powder has all the temperature characteristics for injection or extrusion molding. Most satisfactory compression results are obtained by using 20° to 50°F. higher mold temperatures than are required for general-purpose Lucite.

Good extrusion results are obtained by using a short screw and a low screw speed, preferably 5 r.p.m. or less. Stock must be thoroughly dried. A moisture content not exceeding 0.02 per cent is necessary for best extrusion results. Machine cylinder temperatures are from 30° to 50°F. higher than for general-purpose Lucite.

PHYSICAL PROPERTIES OF MOLDED HEAT-RESISTANT "LUCITE" (FORMULA HM-119) AND GENERAL-PURPOSE "LUCITE" (FORMULA HM-102)

Property	Test Method	Heat-Resistant "Lucite" HM-119	General-Purpose "Lucite" HM-102
Mechanical Properties			
Tensile strength, 77°F, psi (min)	ASTM D638-42T	7,000	7,000
Elongation (min)		1%	1%
Tensile strength, 170°F, psi (min)	ASTM proposed method	2,900	2,200
Elongation		49%	
Modulus of elasticity, 77°F, psi (min)	ASTM D638-42T	400,000	400,000
Flexural strength, 77°F, psi (min)	ASTM D650-42T	15,000	15,000
Impact strength, Charpy, 77°F, ft-lb/in. of notch (min)	ASTM D256-41T	0.35	0.35
Rockwell number (min)	Note 1	100M	80M
Mar resistance	ASTM D673-42T	60%	60%
Thermal Properties			
Coefficient of linear expansion, 0 to 25°C, per °C	ASTM D696-42T	$6\text{–}8 \times 10^{-5}$	$6\text{–}8 \times 10^{-5}$
Thermal conductivity, cal/cm²/sec/°C/cm	ASTM D325-31T	$5\text{–}7 \times 10^{-4}$	$5\text{–}7 \times 10^{-4}$
Btu/ft²/hr/°F/in		1.4–2.0	1.4–2.0
Heat distortion temperature (min)	ASTM D648-41T	72°C (162°F)	64°C (147°F)
	Proposed ASTM method (Note 2)		
	Stress 264 psi	80°C (176°F)	72°C (162°F)
	Stress 16 psi	90°C (194°F)	80°C (176°F)
Yield temperature (min)	Note 3	95°C (203°F)	79°C (174°F)
Flow temperature (max)	ASTM D569-41T	168°C (334°F)	143°C (289°F)
Deformation under load at elevated temperatures (max)	ASTM D621-41T	9%	20%

Property	Test Method	Heat-Resistant "Lucite" HM-119	General-Purpose "Lucite" HM-102
Optical Properties			
Index of refraction	ASTM D542–42	1.49	1.50
Light transmission, total visible (min)	Physical photometer illuminant C	90%	90%
Molding Properties			
Molding temperature, compression		300–350°F	250–300°F
Injection		430–490°F	300–375°F
Molding pressure, psi compression		2,000–7,500	2,000–7,500
Injection		15,000–30,000	10,000–25,000
Miscellaneous			
Specific gravity		1.19	1.17
Water absorption (max)	ASTM D570–42	0.4	0.4
Tendency to cold flow		Slight	Slight
Burning rate		Very slow	Very slow
Effect of age		Practically none	Practically none
Effect of sunlight		Practically none	Very slight

NOTES

(1) The M scale specifies a ½ in. penetrator and a 100-kg load. The major load was removed within 1 sec after fully applied, and reading was made 30 sec later.

(2) The proposed ASTM method differs from ASTM D648–41T in that the sample is immersed directly in oil during the test and in that the temperature is raised at 2°C per minute, four times the standard rate. The fiber stress is 264 psi in the proposed method as in the standard method. The data given at 16 psi were obtained as above except for use of a smaller load.

(3) The yield temperature is the temperature at which an injection molded test bar 2½ in. × ½ in. × 0.050 in. loaded as a cantilever beam with fiber stress of 2 psi deforms 0.060 in. when immersed in an oil bath, the temperature of which rises at 2°–3°C per minute.

NEW HIGH IMPACT PHENOLIC

A high impact phenolic, developed by Bakelite Corporation, is a black material having a string filler, rather than chopped fabric used for most other types of shock-resistant materials. Impact strength of this new phenolic, which is designated BM-16468, is about 20 to 25 times greater than general purpose phenolics.

Molded test specimens indicate that this new material has the following physical properties:

PHYSICAL PROPERTIES

	Direction of Stress	
Compressive strength, psi	Parallel	27,500–32,700
	Transverse	15,600–18,000
Tensile strength, psi	Transverse	7,500–8,500
Flexural strength, psi	Parallel	12,000–12,900
	Transverse	10,200–14,200
Maximum deflection, in.	Parallel	0.086–0.122
	Transverse	0.095–0.118
Impact strength, Izod, energy to break, ft-lb per in. notch	Parallel	3.49–4.84

IMPROVED PHENOLIC MATERIAL

General Electric Company has developed an improved phenol-formaldehyde plastic, known as G-E Textolite 1420. This is a casting material which is being used for making hydro press blocks, drill jigs, checking fixtures and stretch forming dies. It is said to have made an important contribution to aircraft tooling by making possible the use of plastics drill jigs and forming dies, thus conserving vital metals.

It has several important advantages. For one thing, it is light in weight, having a specific gravity of 1.35. It is inexpensive, easy to use and to machine, durable, resistant to moisture and oils and dimensionally stable when completely cured. By varying the amount and type of filler, the properties can be modified to meet a wide variety of requirements.

IMPROVED POLYSTYRENE MATERIAL

Since 1940, General Electric Company has developed a modified polystyrene material with unusual characteristics. This material,

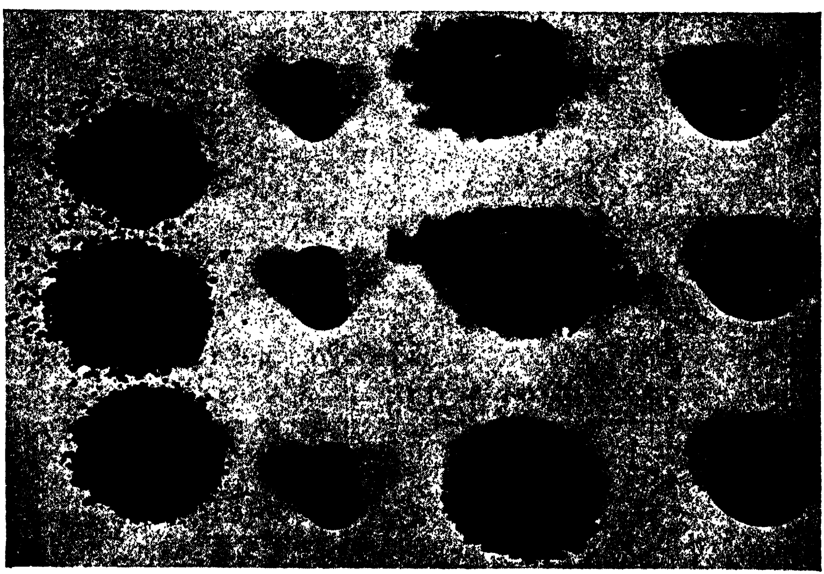
known as G-E 1421, withstands high temperatures without melting, has high dielectric strength, low power factor and low dielectric constant. It has been used in the radio industry in some cases where other materials have not proved satisfactory.

Cast in the form of rods, G-E 1421 has the following properties:

Color	Pale yellow to water white
Machinability	Good, similar to brass
Specific gravity	1.04–1.06
Impact (Dynstat)	0.07–0.08 ft-lb
Flexural strength	(Dynstat) 7500–10,000 lbs psi
Water absorption	Less than 0.1% in 24 hr
Dielectric constant	2.4 to 2.5
Power factor	0.0006–0.0009
Solvent resistance	Generally insoluble in most solvents but swells in aromatic hydrocarbons

IMPROVEMENT IN UREA RESINS

American Cyanamid Company has recently developed a new "stripping" grade of Beetle designed primarily to aid in speeding



Courtesy Anchor Hocking Glass Corp.

Fig. 15. This shows four steps in production of some closures. At the left is loose powder, then the pressed preform, third the molding with flash and at right the tumbled finished product.

the mass production of molded caps and closures. This makes available for the first time a urea-formaldehyde molding material that also has sufficient temporary elasticity to permit ejection of the molded pieces from the threaded male die or force plug without unscrewing.

Thus, to the other advantages of urea-formaldehyde resins — chemical inertness, light weight, durability and availability of a wide range of colors — is added the "stripping" advantage, which contributes materially to the production efficiency of modern molding techniques.

A leading molder reports that the new "stripping" compound results in only approximately 1 per cent rejections.

Bakelite's recent improvements in ureas have produced materials with greater toughness and higher operating temperatures.

Courtesy Celanese Plastics Corp.

FIG. 16. These Lumarith funnels and graduates are resistant to food acids and many other chemicals.

IMPROVED CELLULOSE MATERIALS

Hercules Powder Company, Inc., reports that higher quality raw materials plus more exacting manufacturing control has resulted in better color and opacity for the entire cellulose group. The color of cellulose acetate has been improved as has also the sheet stock opacity. Some high quality cellulose acetate, which has a color value of 0.50 and opacity of 0.14, has been prepared in the laboratory. The mere development of this material indicates some of the future possibilities in the cellulose acetate field.

The production and increased use of high-acetyl cellulose acetate has been a leading feature in the development of more dimensionally stable water-resistant plastics. Outstanding in this field is the use of acetate of over 58 per cent acetic acid for paint brush bristles.

IMPROVEMENT IN CASEIN PLASTICS

The only improvement in the casein type of plastics which has occurred over the last few years is the development of materials with pearl-like effects. These materials do not represent any change in the chemical composition of the casein formula but rather new forms of processing.

The pearl-like materials have been welcomed by the button manufacturers not only for their beauty, but because the importation of ocean pearl shell from the Far East has been limited.

CHAPTER V

New Fibers

FIBERS

THE four principal textile fibers in use in 1940 were cotton, wool, silk and rayon. Of these, only rayon is a man-made fiber. It is a cellulosic fiber made from cotton or wood pulp.

In 1940, the new man-made fibers, such as nylon, Vinyon, Aralac and soybean fibers, had been developed but were not commercially established. For this reason their effects on total fiber consumption were negligible.

The accompanying table shows the per capita consumption of cotton, wool, silk and rayon since 1911. Figures vary from year to year, but show remarkable stability from decade to decade. Total consumption for the four principal fibers averaged 31 lb. per capita annually in the decade 1931 to 1940, which was virtually the same as the annual average of 30 lb. from 1921 to 1930, and 31 lb. from 1911 to 1920. Apparently, increased consumption of fibers for industrial purposes has just about been offset by decreased use resulting from the trend toward lightweight clothing.

In general, the demand for textile fibers is relatively inelastic. Over a period of years the gains made by one fiber are offset by the losses of another. Thus, per capita consumption of rayon increased over 2 lb. between the decades 1911 to 1920 and 1931 to 1940, but cotton showed a corresponding decline. Introduction of nylon in 1940 was immediately reflected in lower silk consumption.

Per capita consumption of rayon has increased from 0.02 lb. in 1911 to 4.62 lb. in 1942, but it still accounts roughly for about 10 per cent of the total consumption of the four principal fibers.

It seems almost inevitable that, as rayon is improved and other man-made fibers become established, the natural fibers, cotton, wool and silk will decline in relative importance. Silk will in all probability be among the most seriously affected. Many research

men believe that silk may disappear from the American market. The decline in importance of cotton and wool will no doubt be a slower process.

Cotton accounts for over 80 per cent of total fiber consumption and will probably not suffer any serious displacement for some time,

PER CAPITA CONSUMPTION OF FIBERS IN U.S.

Year	Cotton (a) lb	Wool (b) lb	Silk (c) lb	Rayon (d) lb
1942(e)	39.2	4.48		4.62
1941	40.8	4.86	0.19	4.40
1940	35.8	3.09	0.36	3.69
1939	29.2	3.03	0.42	3.50
1938	25.9	2.19	0.44	2.52
1937	22.1	2.96	0.50	2.39
1936	30.2	3.17	0.53	2.52
1935	24.3	3.28	0.57	2.03
1934	20.6	1.82	0.48	1.56
1933	22.3	2.53	0.56	1.73
1932	24.0	1.84	0.60	1.24
1931	19.2	2.51	0.71	1.28
1930	20.6	2.14	0.66	0.97
1929	24.3	3.02	0.80	1.10
1928	28.3	2.76	0.72	0.83
1927	27.6	2.97	0.71	0.84
1926	29.4	2.92	0.65	0.52
1925	26.4	3.02	0.66	0.50
1924	25.7	3.00	0.52	0.37
1923	23.9	3.77	0.55	0.29
1922	28.8	3.69	0.52	0.22
1921	25.7	3.16	0.48	0.18
1920	22.0	2.95	0.36	0.08
1919	29.3	3.13	0.52	0.09
1918	26.6	3.82	0.46	0.06
1917	30.3	3.33	0.42	0.07
1916	31.8	3.55	0.40	0.06
1915	30.6	3.35	0.37	0.06
1914	27.2	2.74	0.31	0.05
1913	27.5	2.35	0.35	0.04
1912	27.7	2.92	0.31	0.03
1911	26.2	2.64	0.28	0.02

(a) Year beginning Aug. 1, 1914, to date; year beginning Sept. 1, 1911—1913.
(b) Apparel and carpet wool, reduced to scoured basis; on calendar-year basis.
(c) Net imports, 1911 to 1933; imports for consumption, 1934 to date, on calendar-year basis.
(d) From Rayon Organon. Includes filament yarn and staple fiber. Calendar-year basis.
(e) Preliminary.

Bureau of Agricultural Economics. Calendar-year figures divided by July 1 population estimates to get per capita figures. Crop-year figures (for cotton) divided by January 1 population estimates to get per capita figures.

although it will continue to lose ground here and there to rayon and other synthetics.

There is no satisfactory substitute for wool. Casein fiber (for example, Aralac), sometimes called "synthetic wool," is far from possessing all the qualities of natural wool. Staple-fiber rayon, however, has been substituted for wool in several of its applications and may become more of a competitive threat in the future. Other wool substitutes are being investigated.

Perhaps the most promising of the newer synthetic fibers thus far introduced is nylon. It was put on the market by the du Pont Company in 1940 and immediately found wide public acceptance for women's hosiery. At the end of 1940 nylon stockings were being manufactured at the rate of 68,000,000 pairs annually, and in 1941 109,000,000 pairs were made. Nylon was also used for many other products before output was diverted to military uses such as parachutes, glider tows, tire carcasses, etc. After the war, however, the steep uptrend in civilian demand for nylon should be resumed.

Some of the other new fibers, such as Vinyon, Velon and Aralac, have just emerged from the development stage. Their growth after the war should be rapid.

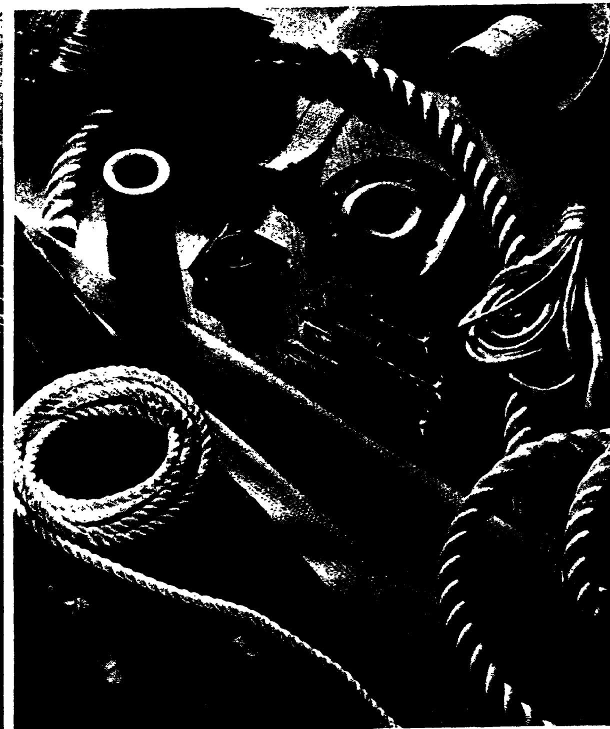
NYLON FIBER

Two kinds of nylon yarn are made today, standard yarns and high-tenacity yarns. These are available in a range of deniers from 20 to 210 and can be produced as either bright yarn or semi-dull yarn containing a delusterant. Tenacities for these yarns range from 4.5 to 7.0 g. per denier depending on the denier and the type yarn supplied.[1]

The standard and high-tenacity nylon yarns contain filaments, each approximately 3 denier. Other types of yarn are made with the filament-denier ratio as high as 9 and the weight as low as 1.5 denier per filament. The individual filaments of nylon yarn are cylindrical, smooth and uniform and behave in a different manner from most other fibers. They may be twisted into a yarn, with or without water-removable adhesive size and oil. The size acts much

[1] At this point, it may be helpful to explain that a denier is a measure of weight for fibers. A 1-denier filament is by definition of such length that 9000 m. weigh 1 g.

Fig. 17. This shows the diversity in application of nylon plastics.



Courtesy E. I. du Pont de Nemours & Co., Inc.

Fig. 18. Nylon yarns and filaments are looking to a wide postwar market.

the same way as "sericin gum" on raw silk. It binds the filaments of the yarn together during the textile knitting and weaving operations and is removed when the nylon fabrics are scoured and finished. Standard yarns have a tenacity of 4.5 to 4.8 g. per denier and elongations of 18 to 22 per cent before breaking. Forty-denier nylon has a breaking strength of approximately 0.4 lb. and 60-denier 0.6 lb. When stretched for short periods, nylon yarns possess about 8 per cent true elasticity, that is, nylon yarn that is stretched about 8 per cent of its original length will return to its original length; if, however, nylon is stretched much more than this, it will not recover quite the entire stretch, but will be slightly elongated permanently.

High-tenacity nylon yarns have a tenacity of 6 to 7.0 g. per denier and an elongation of 11 to 17 per cent. They are put up as 30 denier 10 filament, 70 denier 23 filament, 105 denier 34 filament, or 210 denier 68 filament. Filament size and structure are similar to standard yarns. The minimum breaking strength of 210 denier is approximately 2.8 lb.

Nylon yarns absorb about 4.75 per cent moisture at 72 per cent relative humidity, and 7 to 8 per cent moisture at 100 per cent relative humidity. This low moisture absorption enables nylon yarn to dry quickly and minimizes swelling and weakening when wet. The wet (saturated) strength of nylon yarn is approximately 85 per cent of its bone-dry strength.

Nylon yarn is solid, dense and still light in weight, having a specific gravity of 1.14 as compared with silk at 1.30, viscose process rayon at 1.52 and acetate rayon at 1.30.

Physical Properties. *Tensile Strength and Elongation.* Nylon yarn can be manufactured so that it will have a relatively high or a low tenacity, as desired. The lower the ultimate (breaking) elongation of nylon yarn, the higher is the tenacity for any given type of nylon. Currently, types of nylon yarn are being made that range from approximately 4.5 to 7.0 g. per denier tenacity with corresponding average elongation ranges of 20 to 12 per cent (as determined at 72 per cent relative humidity). As previously mentioned, the tenacity of thoroughly wet nylon is approximately 85 per cent of its dry tenacity, ranging from 84 to 90 per cent, 72 per cent relative

humidity, while the elongation of wet nylon is 5 to 30 per cent greater than that of the dry nylon measured at 72 per cent relative humidity.

The following are examples of average properties of current yarns:

Bright Yarn				
Denier	*Filament Count*	*Twist and Direction*	*Average Tenacity Grams per Denier*	*Average % Elongation*
30	10	1Z	5.7	20.0
40	13	1Z	4.7	18.5
60	20	1Z	4.8	20.0
210	68	1Z	6.4	15.5

Chemical Resistance. Nylon polymer (flake) or yarn is substantially inert to virtually all organic acids, carbon bisulfide, halogenated hydrocarbons, carbon tetrachloride, trichlorethylene, alkalies (NaOH), soaps, gasoline, benzene, benzine, aldehydes, ketones and alcohols. The outstanding exceptions are formic and carbolic (phenol) acids, the latter being *solvents* for nylon. Other solvents for nylon at 77°F. are meta-cresol, cresylic acid and xylenol.

Nylon yarn is degraded (made to lose strength) by oxidizing agents and by mineral acids such as hydrochloric and sulfuric. Boiling in 5 per cent hydrochloric acid makes nylon brittle and ultimately causes complete disintegration. Cold concentrated nitric acid rapidly disintegrates nylon.

At room temperature approximately 16 per cent of the strength is lost when yarn is immersed in hydrochloric or sulfuric acid for 10 min.

Sodium hydroxide of 10 per cent concentration at 185°F. for 16 hr. caused no apparent degradation of nylon.

Abrasion Resistance. Nylon yarn has high resistance to abrasion. For example, all-nylon hose or nylon used as reinforcing thread in the toe and heel gives wear that is superior to silk, rayon or cotton in the foot areas. Nylon hose have consistently shown two to two and one-half times the wear life of comparable gauges and weight of all-silk hose.

The resistance is attributed to the inherent toughness, natural pliability and the ability of nylon to undergo a high degree of

flexing without breakdown. Coupled with these properties, the smooth filament surfaces do not readily create friction when rubbed against themselves or other surfaces.

These inherent characteristics can best be illustrated by the experience with nylon brush bristles. The ratio of the life of nylon toothbrush bristles to that of natural bristles has been about three to one.

Nylon bristles have also lasted three to four times as long as natural bristles used in bottle-washing machines. Used as a "furnisher brush" in the textile printing industry, the original nylon brush was still in active service after a year's operation while natural bristles in some cases lasted only a week. Other places where nylon-bristled brushes have shown outstanding wear resistance are in sewage-disposal plants, vacuum cleaners, dairies, electroplating and porcelain enamel equipment.

Fiber	*Density*
Nylon	1.14
Silk (raw)	1.30–1.37
Silk (boiled off)	1.25
Wool	1.30
Cotton and linen	1.50
Viscose, cupra, rayons	1.52
Acetate rayons	1.30
Ramie	1.52

Density. From the above data it appears that nylon yarn should be bulkier and give more coverage than any other common textile fiber for thread of a given weight. In most uses the exact opposite is true. First, nylon is comparatively translucent, particularly in the low-twist bright-yarn form.

Secondly, the thread is extremely compact because each filament is uniformly circular in cross section and is free from surface irregularities, being similar to glass rods in this respect. Thus nylon hose possess greater sheerness than silk hose of comparable gauge and weight.

When nylon is compared with materials outside the textile field, such as copper wire, its advantage in light weight shows up quite markedly. For instance, where nylon wire (specific gravity 1.14) is

substituted for copper wire (specific gravity 8.9), as in industrial filter screening, equal weights of these two materials will result in a much greater yardage of finished nylon screening.

Elastic Recovery. Elastic recovery is the ability of a material to regain its original length after being stretched. Without elastic recovery, it is not possible to produce fabrics that will maintain their original shape or conform to specific contours of the body. The cling or fit of nylon and silk hose results from the inherent elastic recovery of these two fibers.

The elastic recovery for various materials at various conditions is outlined below:

(a) Recovery against no load, stretch 100 sec. recovery within 60 sec.

% Stretch	*% Elastic Recovery*	
	Silk	*Nylon*
2		100
4	76	100
8	56	100
16	47	91

(b) Recovery against a load of 0.25 g. per denier stretch for 30 sec. recovery in 60 sec.

	After Stretch of		
	1%	2%	4%
Nylon	38%	63%	73%
Silk	82%	74%	59%

Delayed Recovery. When nylon yarn is allowed to relax against no load after it has been held under tension for several days, it does not immediately return to its original length, but creeps back slowly. However, it almost instantly recovers approximately 50 per cent of the stretch imparted and will during the first 24 hr. recover a total of approximately 85 per cent of the amount of stretch. It will require approximately two weeks for the stretched yarn to recover completely and return *to its original length.* These results were obtained from yarn held under constant relative humidity conditions of 72 per cent.

Stretchability — Modulus of Elasticity. Nylon yarn requires only

about one-third or one-fourth as much tension for a given amount of stretch as silk, and requires less tension than wool or cotton. (This refers to unsized nylon; the effect of size on modulus varies with the amount and type of size material.) This is illustrated by the following table:

COMPARATIVE TENSIONS THAT WILL STRETCH EACH OF SEVERAL COMMON FIBERS 1 PER CENT

Unshrunk nylon	0.25 gm/den
Shrunk nylon	0.10–0.15 gm/den
Silk	0.75–1.16 gm/den
Wool	0.32 gm/den
Cotton	0.50 gm/den
Glass yarn	2.75 gm/den
Cellulose acetate	0.40 gm/den
Viscose rayon	0.70 gm/den
Ramie and cuprammonium	0.90 gm/den

The ease of stretching nylon increases greatly with an increase in relative humidity. This is illustrated by the following table:

AMOUNT OF TENSION PER 1 PER CENT STRETCH, FOR STRETCHING UNSIZED NYLON AT VARIOUS RELATIVE HUMIDITIES

0.48 gm/den	0% rel hum
0.31 gm/den	50% rel hum
0.116 gm/den	100% rel hum

The tables show wide variations in the stretchability of nylon corresponding with variations in relative humidity. They also show that the thread tension should be as uniform as possible in order not to introduce large variations in the amount of stretch. Nylon should be handled as if it were a rubber yarn. Although it possesses elasticity, like rubber, nylon yarn does not recover or snap back after release of tension as quickly as rubber. Like rubber, it constantly tries to return to its original length when held under stretched condition and will exert appreciable contracting force upon any packages on which it is wound.

It possesses sufficient contracting force to crush partly the cores of cones and the maple barrels of bobbins.

In view of the crushing force exerted by nylon yarn it is extremely

important that tensions employed in winding cones, spools, bobbins or beams, etc., be held to a minimum consistent with proper performance and that consideration be given the quantity of yarn per unit package. The more wraps the package contains the greater the potential crushing force.

Flammability. Experiments have shown that nylon yarn exceeds silk, rayon and cotton in resistance to burning. These facts were confirmed by tests on woven fabrics conducted by the Associated Mutual Fire Insurance Company.

Undyed, finish-free nylon yarn will melt at a temperature of approximately 482°F. if a flame is applied. As soon as the flame is removed, however, the melt will harden with little or no tendency for further flame propagation. The term "flameproof" as applied to fabrics implies a resistance to any spread of flame after the fabric has been ignited. Undyed unfinished nylon yarn may, therefore, be considered flameproof since it does not support spread of the flame after the igniting source has been taken away from the material. Cotton, paper and wood are distinctly different in this respect.

If flammable oils or finishes are present on the fiber, it is always possible that the resulting treated yarn will support combustion because of their presence. Pigments and dyes may also cause the flame to spread along the fiber. If pigments, dyes or even contaminating salts release oxygen on ignition faster than the rate at which oxygen necessary for combustion can be obtained from the air surrounding the ignited material, they will speed up the burning of nylon and/or other materials on which they are present.

Heat Resistance and Related Properties. The average "heat capacity" of nylon between 20°C. (68°F.) and 250°C. (482°F.) is 0.555 calories per g. per °C.

Its heat of fusion is 22 calories per g.

The resistance of nylon to deterioration due to heat may be summed up as follows:

100°C (212°F) — exposure to steam for 6 days produced appreciable change in tenacity.

65°C (149°F) — air at this temperature (stored in the dark) causes about 5% loss in tenacity after 4 months' storage.

65°C (149°F) — air at this temperature (stored in the dark) causes about 20% loss in tenacity after 1 year's storage.
200°C (392°F) — in an oxygen-free atmosphere for 3 hr — no change in tenacity.
225°C (437°F) — in an oxygen-free atmosphere (nitrogen), heating for 1 to 3 hr — causes some decrease in strength and at 245°C (473°F) considerable loss in strength.

Ironing. No effect on tensile strength for iron temperatures up to 356°F. (180°C.). At 275°F. (135°C.) unset creases are removed; at 356°F. sticking begins. At 446°F. (230°C.) damage starts.

Three important factors in ironing are the pressure applied, the time of contact of iron with surface of fabric and the amount of moisture present in the fabric or in any covering cloth.

Heat Yellowing. After heating for 5 hr. at 302°F. (150°C.) in dry air the relative color change of a series of undyed fabrics was:

Silk — Brown
Wool — Yellow
Nylon — Light yellow
Viscose and acetate rayon — Still lighter yellow
Cotton — Very slight yellowing — barely noticeable

Effects of Extreme Cold. Standard and high-tenacity yarns show no loss in tenacity and only slight decrease in elongation when "chilled with dry ice" (sublimation temperature about −112°F.). Nylon rope also showed no loss in strength when conditioned at −40°F. for as long as 6 hr. and retained its original strength upon being reconditioned at normal temperatures.

Resistance to Attack by Insects. Tests indicate that nylon is subject to damage or eating of the fiber by some insects. Proper packing and conditions of storage should therefore be adhered to.

Clothes moths endeavor to cut their way out of scoured nylon cloth when trapped or imprisoned in the folds, causing moderate damage. Neither the larvae nor the moths appear to eat the nylon for food as they do in the case of wool.

Black carpet beetles damaged nylon and silk by cutting the fibers in an effort to release themselves.

Firebrats slowly cut their way out of nylon and silk fabric, if imprisoned.

Certain varieties of ants in some localities of the United States cut their way out of nylon, silk and other fabrics when imprisoned.

Resistance to Fungi and Microorganisms. Undyed, unfinished nylon yarns and fabric have been found to be remarkably resistant to molds and other microorganisms showing insignificant loss in strength after severe exposure to *Chaetomium globosum*, *Metarrhizium*, *Stachybotyrs sp. Aspergillus* and *Penicillium* and to microorganisms (particularly the cellulose-destroying organisms) encountered in a soil-burial test. Fabrics exposed to soil-burial tests for 21 days retained from 95 to 99 per cent of their original strength and were relatively bright and clean after rinsing in cold water. Cotton fabrics exposed under identical conditions were completely destroyed.

Molds. Molds can be induced to grow upon nylon yarn by applying suitable food materials, but such growth causes little if any loss in strength of the yarn. The use of certain finishes on nylon fabric might induce or support the formation of mold on the finish. Each finish should be individually tested to determine possible reaction.

Bacteria. Controlled tests have shown that bacteria of any kind do not readily attack nylon.

Resistance to Marine Deterioration and Fouling. Nylon fishing lines, both waterproofed and unwaterproofed, when exposed to both fresh and salt water intermittently for a period of 6 months lost only about 20 per cent of their original tensile strength.

During this period waterproofed line accumulated a 4- or 5-in. growth of marine moss which was apparently feeding on the waterproofing material, as the unwaterproofed line was perfectly clean.

Influence of Light. Nylon yarn, like other textile fibers, is subject to degradation on exposure to sunlight. Nylon resistance to deterioration by sunlight depends on the type of nylon and other factors, that is, whether it is bright or pigmented semidull, the season when exposed, the temperature and humidity during exposure, the thickness of the yarn or other material, whether it is exposed outdoors or behind glass and the length of exposure time.

In general, either bright or pigmented semidull nylon yarns are superior to silk in resistance to deterioration under identical conditions of unprotected exposure 45° south for 14 days in Florida sun-

light. Bright nylon is equivalent to either carded or combed cotton under these same exposure conditions. The silk and nylon samples were given a thorough scour prior to exposure.

A similar test made in Wilmington on unprotected samples exposed to direct sunlight 45° south for 16 weeks again showed the superiority of nylon over silk as follows:

Yarn	*% Loss*	
	Tenacity	*Elongation*
Average for pigmented semidull nylon	50	60
Average for bright nylon	23	25
Average for silk	85	82
Average for linen	23	24
Average for glass yarn	37	0
Average for high tenacity, viscose process rayon	20	21
Average for cotton	18	25

Finish-free samples of semidull nylon stored in the dark under normal room temperatures showed no loss in strength during 9 months' storage. High-temperature conditions in the range of 150°F. would alter this slightly, as illustrated by storage of bright nylon in the dark at 149°F. (65°C.) for 16 weeks, which resulted in a negligible loss of 2 per cent in strength.

Hosiery fabrics from semidull nylon stored for two and one-half years in a closet at room temperatures have shown no apparent losses in strength.

Curtains of nylon hung in office windows facing northwest have shown no evidence of deterioration in a year's time.

Outdoor exposure tests on comparable samples of nylon and manila rope show that both lose strength on a percentage basis at about the same rate. However, the nylon rope remains definitely stronger and has the same percentage of advantage over manila at the end of a year of atmospheric exposure.

Moisture Regain. The moisture regain of nylon at any given relative humidity is considerably less than that for other textile fibers such as silk, cotton, wool, viscose rayon or acetate rayon. For example, the moisture regain of nylon at 65 per cent relative humidity is

approximately 3.8 per cent, compared with values of 11 per cent for silk, 7.5 per cent for cotton, 11 per cent for mercerized cotton, 16 per cent for wool, 12 per cent for viscose rayon, 6 per cent for acetate rayon and 8 per cent for linen.

The rate at which a given package of nylon yarn will pick up or lose moisture is dependent upon the type of package to which it is wound, particularly the density of the package. Packages originally at equilibrium with 72 per cent relative humidity which were transferred to an atmosphere of 50 per cent humidity reached equilibrium as follows: cones, approximately 300 hr., spools, approximately 320 hr., shipping bobbins practically no change after 530 hr.

The time required for nylon unsized unfinished fabric either saturated at 100 per cent relative humidity or essentially dry to reach equilibrium at 72 per cent relative humidity was approximately 20 min. under both conditions; 450-meter skeins took 60 to 85 min. to reach equilibrium. This would indicate, therefore, that any conditioning treatment should be dependent upon the type of package. For instance, the conditioning of cones should probably cover a period of at least 2 days.

The low moisture regain of nylon as compared with rayon, silk or cotton makes the yarn more susceptible to the accumulation of static electricity. The relative humidity of the atmosphere should therefore be maintained at as high a level as is consistent with good performance of the particular operation involved.

Shrinkage and Swelling. Water, glycerin, and a 10 per cent sodium hydroxide solution at room temperature cause no lateral swelling of nylon fibers. Boiling with 10 per cent Glauber's salt causes a 3 per cent swelling.

The wet length of nylon varies from about a 3 per cent gain to an actual loss in length as compared with bone-dry nylon, depending upon the degree of previous relaxation and removal of residual shrinkage. Fully shrunk nylon yarn gains in length when wet.

Sized and oiled and twist-set[1] yarn showed the following shrinkage characteristics under the conditions listed below.

[1] Twist-setting conditions — Wet Bulb 160°F — Dry Bulb 170°F. Relative Humidity 75%, time 1.5 hr.

Treatment	*% Yarn Shrinkage**
25°C (77°F) in water for 3 min	0
50°C (122°F) in water for 3 min	0.2
75°C (167°F) in water for 3 min	0.5
100°C (212°F) in water for 3 min	2.8
100°C (212°F) in steam for 3 min	0.2
100°C (212°F) in steam for 10 min	0.5
100°C (212°F) in steam for 30 min	1.4
120°C (248°F) in steam for 3 min	2.4
120°C (248°F) in steam for 10 min	2.5

*Shrinkage of twist-set yarn is dependent on the particular tension used in winding the packages prior to twist-setting treatment.

This indicates that boiling water is more effective for shrinking than steam at atmospheric pressure.

Nylon yarn immersed in 5 per cent cresylic acid solution for 5 to 10 min. at 122°F. shrank to almost one half of its original length.

The unrelaxed residual shrinkage (total shrinkage) of a shipping bobbin is approximately 8 to 11 per cent. For yarn not twist-set on size bobbins, spools or cones the values lie somewhere between 6.5 and 8.5 per cent. Twist-set yarn has 1 to 4 per cent unrelaxed residual shrinkage.

Water Extractable Material in Nylon. When nylon is given to scour to remove size and/or oil, there is a slight loss of water-soluble material in the nylon itself. The amount of this loss is related to the temperature, time and constituents (soap or plain water) of the scour bath.

Under a very specific set of scour conditions approximately 1 per cent of extractable material was removed in addition to size and oil. More drastic boil-off procedures may result in a slightly greater loss, whereas less drastic procedures approaching something like soaking in water at room temperature may result in a lower loss of extractable material.

This is a basic characteristic of nylon and apparently does not indicate weakening of the fiber. Rayon also loses certain extractables during a scour.

Net billed weights do not take into account this loss, since the billing factors are arrived at by an oil analysis involving extraction with ether or xylene, and titration for size content. Neither of these analytical steps will remove extractable materials.

This reduction in weight is taken into consideration in the pricing of the yarns and should be considered as a part of the "working loss."

ARALAC

Developed after years of research by National Dairy Products Corporation, Aralac is the first natural protein fiber to be produced commercially in the United States. Made from casein of skim milk, it is sometimes called "synthetic wool" because wool also has a protein base, in contrast to the cellulose base of cotton or rayon.

Casein fiber was used extensively in various foreign countries, particularly Italy, for some years before the war, as a substitute for the natural wool they lacked in sufficient quantities to meet their needs. The Italian variety of casein fiber was known as Lanital. Other countries had distinctive names for their fibers. Aralac, however, is believed to be superior to the other casein fibers.

Annual production of whole milk in this country has been around 120,000,000,000 lb. The separation of cream or butterfat from whole milk for creamery butter and table cream requires about half of all the whole milk produced, and from 50 to 55 billion lb. of skimmed milk remain after the cream has been removed for butter and table cream. The great bulk of this skim milk never leaves the farm (since the farmers do most of the separating themselves) and its principal use has been for animal feed.

For years scientists of the U. S. Department of Agriculture and research laboratories of dairy companies have been endeavoring to find new uses for skim milk. As a result of these research efforts, skim milk has been processed into powder and used in flavored milk drinks. The casein has been used to make coated paper, paints, buttons, other plastics and glues. But around three quarters of the skim-milk supply still remains without a normal, reliable commercial market, and one of the most promising new uses appears to be casein fiber.

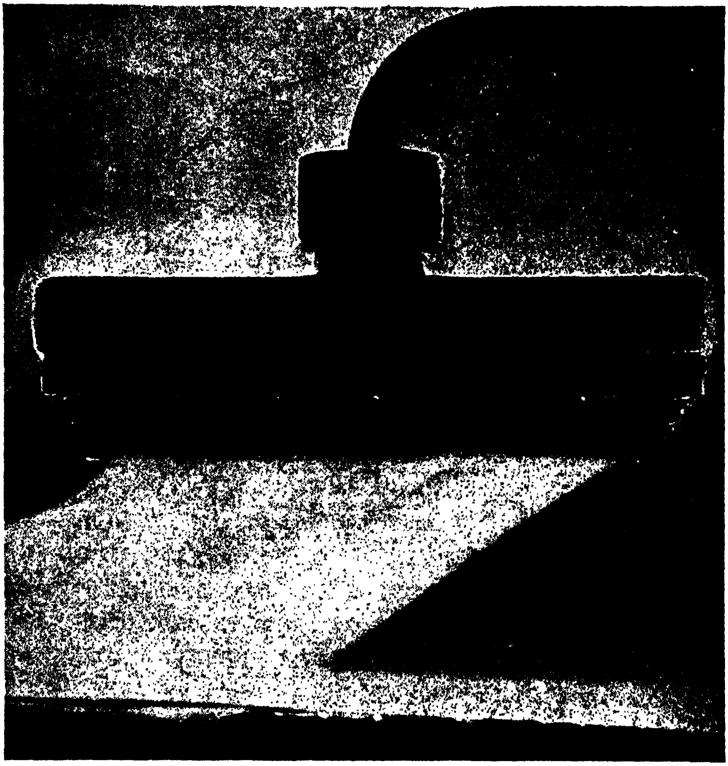
In the production of the fiber, casein is ground into powder form, thoroughly mixed with several chemicals and then extruded through spinnerets (metal cylinders containing thousands of extremely small holes). The thousands of tiny strands that come

Courtesy National Dairy Products Corp.

FIG. 19. This shows Aralac fibers in process. Spinnerets are concealed under the foam.

from the spinnerets merge into a ropelike tape known as "tow." The tow goes through several chemical treatments as well as washing and rinsing processes and is then dried and cut into various staple lengths. The fiber is then baled in 500-lb. lots and is ready for the yarn-spinning mill.

All woven or knitted fabrics are of course made from yarn. Aralac is designed as a blending fiber, and a predetermined



Courtesy National Dairy Products Corp.

Fig. 20. This shows Aralac fiber as it comes from the spinneret.

amount, together with a quantity of rayon, wool or cotton staple, or a combination of any of these, is placed in the blending room. The fibers are then thoroughly mixed by a machine known as the "picker." Then the mixed fibers are drawn into strands which are constantly combed, twisted into ropelike lengths, then combed out again and twisted into lengths of continuously decreasing thickness or diameter until a fine strand of blended yarn results. This single strand is actually a uniform mixture of casein and other fibers and may be used for weaving or may be "plied," that is, twisted together with other yarns, before it is put in the looms.

The looms at the weaving mill control the actual construction of the cloth and the woven cloth is known as "greig goods" — cloth

not yet dyed or finished. The finishing is usually done by a converting house, which dyes the fabric and gives it a final finish before it is sold to the garment manufacturer.

Almost the only application in which Aralac is used unblended is in woven interlinings for women's winter coats. In other uses, which include a wide variety of textiles, the Aralac content in the finished cloth ranged from 20 to 50 per cent in 1943 compared with 20 per cent in 1942. Increased percentages are expected with further research.

Among the applications of Aralac in blended form are dress fabrics, suitings, coatings, sportswear, men's and women's hats, children's clothing, sweaters, snow suits, ankle socks, housecoats and robes, men's ties, quilted garments, comforters and garment interlinings.

Quantity production of Aralac was commenced by National Dairy Products Corporation in January, 1942, and by the end of 1943, productive capacity was at the rate of 9,000,000 lb. annually. The price of Aralac has been $0.64 per lb., which is cheaper than wool but more expensive than cotton and rayon.

The field of application, as well as the proportion of Aralac used in blends, will probably show a gradual growth in the future. Some reduction in price may also be expected as a result of the potential cheapness of the basic raw material used. Increasingly fine diameter fibers are being produced, finer and more uniform than many natural fibers and it is expected that new fabrics with a touch and appearance hitherto unobtainable will eventually be available.

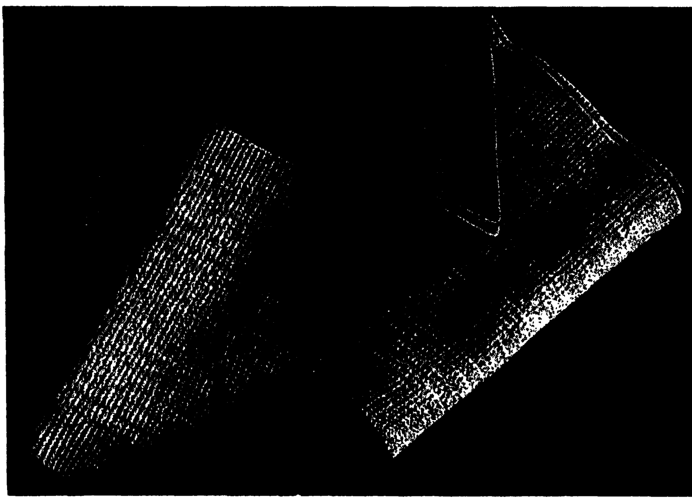
VINYON ELASTIC YARN

A new elastic type of yarn has been developed during the war and is now being used for elastic tapes, webbing and cord. Made of vinyl chloride-acetate resin produced by Carbide and Carbon Chemicals Corporation, the new yarn derives its elasticity from a special plasticizer added to the spinning dope. The new type of Vinyon fiber is thus comparable to the Vinylite elastic plastics, while the older type of Vinyon which has no plasticizing agent corresponds to the Vinylite rigid plastics.

This yarn is one of the first *synthetic* textile fibers possessing high

elasticity. Vinyon elastic yarn can be made with an elongation ranging from 150 to 400 per cent of the original length.

Unlike latex products, which consist of extruded monofilaments, the new Vinyon is a true textile yarn containing a number of parallel filaments. As a result, it has several advantages including an improved feel to cloth woven from it and a greater flexibility. It can be covered, much like latex or rubber products, and it can also be used without covering for special purposes. The yarn itself has a pleasant feel.



Courtesy Carbide and Carbon Chemical Corp.

FIG. 21. Vinyon elastic webbing is used for medical bandages.

Vinyon elastic yarn does not snap back as rapidly when stretched as do rubber or latex yarns. Although this limits its uses somewhat, it results in greater comfort for restrictive apparel applications. Fatigue life as well as resistance to oxidation and acid perspiration are considerably greater than those of rubber. The yarn will withstand boiling in water for as long as 12 hr. without damage but continuous exposure to dry-cleaning solvents and soap solutions causes stiffening. Sulfated alcohol type detergents are recommended for scouring, dyeing or laundering.

The temperature range through which elastic properties are

retained is approximately 0° to 75°C. (32° to 167°F.). Below this, the yarn tends to stiffen and become sluggish, while above this range, it tends to deform permanently when stretched. In general, the elasticity increases as temperature rises.

Because the vinyl resin and plasticizer used were critical, production of the new yarn was first limited to military needs. Such applications included knee braces and elastic tapes for metatarsal pads, elastic tapes for garments for the WAC, and elastic suspension cords for the canopies of jungle hammocks for the Army. Heavy-duty suspenders for aviators' suits were also made and tested.

Among the promising postwar applications are surgical stockings, women's girdles, corsets and foundation garments, elastic tops for hosiery, supporters and suspenders and bathing suits.

VELON

Velon is the name of a new fiber from vinylidene chloride that was introduced by The Firestone Tire and Rubber Company shortly before the war. Its first commercial application was made as upholstery for seats in New York subways. The monofilaments have been produced in diameters ranging in size from 0.007 to 0.100 in. and were finding many new uses before the war.

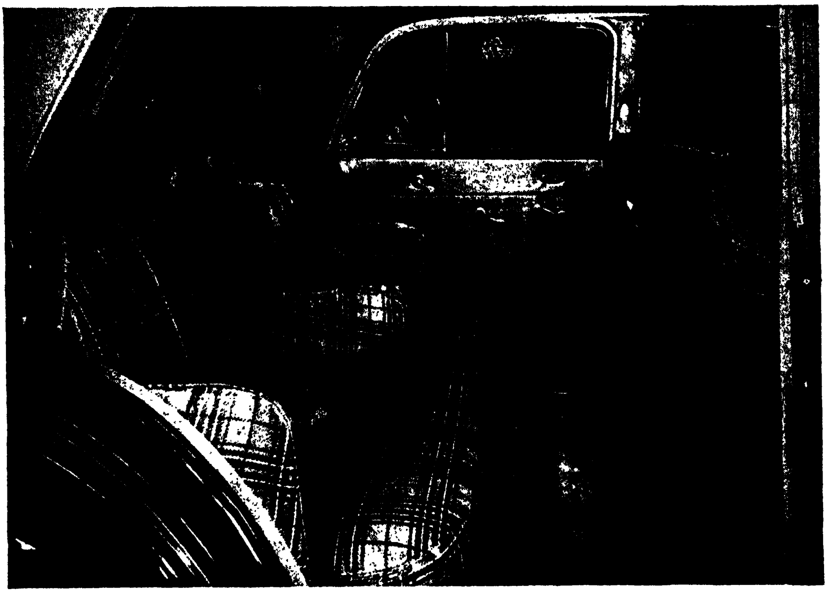
Production of vinylidene chloride fibers was discussed in Chapter III. Here emphasis is placed on Velon and its applications.

Several characteristics adapt Velon to the textile field. It can be made in a wide range of attractive colors and has a lustrous and attractive appearance. It has good tensile and flexural strength. Even more important, it is practically impervious to water, most acids, alkalies and other solvents; it is heat-resistant to all temperatures tolerable to the human body and is not inflammable.

Fabrics made of it have good wearing qualities, can easily be cleaned, and are resistant to attack by termites, moths and vermin. They are only slightly affected by exposure to sunlight, and eventually may be made sunfast.

Fabrics of Velon prove especially valuable for chairs, couches and for outdoor furniture, also for seats in railroad coaches, streetcars, interurbans, buses, automobiles and airplanes. Fabrics can be kept

bright and new looking with a minimum of cleaning effort. No slip covers or seat covers are required. Other uses include window drapes, table cloths, mats and shower curtains.



Courtesy Firestone Tire and Rubber Co.

FIG. 22. Seat covers of Velon are cleaned with a damp cloth. They are said to outlast the automobile.

Velon braids have interesting potentialities for new styling, color combinations and designing. They can be made any width, weight, weave, color or combination of colors. Some likely applications are for trimming women's wear, belts, hat bands, trim and suspenders. An important advantage of Velon is that body perspiration has no effect on it.

Velon is used for making window screens. It does not rust or tarnish and is strong, tough and durable. It is reported to be less affected by temperature and weather changes than metal screen. In the tropics where insects are a scourge, insectproof tents made of Velon have proved satisfactory during the war. Unlike metal screen, Velon can be made in a wide range of attractive colors so that the

home owner or architect can select the proper color to harmonize with the house trim or with the interior drapes or furnishings. Velon screening may be used for industrial purposes in filter plants and the like.

Thus far, Velon fiber has been produced only in the monofilament form, but intensive research is under way to make it into multifilaments, thus broadening its field of application in textiles. According to its maker, it will eventually be produced in the sheerest of gossamerlike weaves for hosiery, lingerie and dresses.

Other items of wearing apparel and accessories for which Velon is well suited are women's handbags in all colors and designs; dress shoes, sport shoes and slippers; outdoor hats and factory headgear for women industrial workers; belts and dress trims; colorful luggage and many other items.

TABLE OF PROPERTIES OF VELON

Specific gravity	1.6–1.75
Refractive index, Nd	1.60–1.63
Tensile strength, psi	Up to 40,000
Elongation, %	25
Flexural strength, psi	Flexible
Resistance to heat, °F (continuous)	170°F
Resistance to heat, °F (intermittent)	Shrinks above 170°F
Softening point, °F	240–280
Tendency to cold flow	Slight
Electrical properties	Good
Water absorption, immersion 25°C	Less than 0.1%
Burning rate	Self-extinguishing
Effect of age	None
Effect of weak acids Effect of strong acids Effect of weak alkalies Effect of strong alkalies	None to slight
Effect of sunlight	Darkens slightly
Effect of organic solvents	Highly resistant
Clarity	Translucent to opaque

POLYFIBRE

Polystyrene fiber (Polyfibre) of the Dow Chemical Company, is a fiber ranging in diameter up to five microns. It is a product of polysytrene, and was first supplied in its simplest form as a bat of

crosswise parallel fibers. The bat width is approximately 14 in. and its length about 10 ft. In this form the material has an apparent density of about 0.05 and contains a small proportion of solvent to facilitate molding.

While restricted to military uses it may have important postwar applications. It is claimed that strong articles having densities as low as 0.4 are possible with Polyfibre and it should benefit from the trend toward light structural materials.

It is well adapted to the application of heat and pressure in fabrication for, being made up of extremely fine fibers, it presents a large surface area per unit of weight. Furthermore, it tends to shrink when subjected to heat and in this way exerts pressure on itself which aids in fabrication.

While Polyfibre was designed principally for further heat application, it has in itself interesting properties as a fiber. The bat is composed of extremely fine fibers, containing many minute air spaces and thus becomes a good thermal insulating material.

Insulating properties and heat absorption might appear to be incompatible, but such is not actually the case. In its use as a thermal insulation, the bat is made up of fibers that are not tightly packed. As a molding bat, however, the fibers are tightly packed and the air is evacuated from the bat. This tight packing and the large fiber surface combine to permit rapid heat absorption and relatively short molding cycles. In addition to excellent thermal insulating properties, Polyfibre appears to be one of the best sound insulating media. This is to be expected, since the slightly compacted fiber bat contains a multitude of interconnected air paths. These relatively long paths offer channels in which sound waves may dissipate their energy.

Polyfibre, like polystyrene in other forms, is difficult to wet. This suggests its application as a replacement for kapok in products requiring buoyancy, such as floats, life vests and emergency rescue equipment. A tendency toward matting may interfere.

There are two general methods of molding Polyfibre. First, and most commonly known, is that of compression or press platen molding. Bulk polystyrene has been molded by the compression method

in the past, particularly when sizes larger than those made by injection molding are desirable.

The use of bulk polystyrene in compression molding is limited because it is a thermoplastic requiring long compression cycles. Polyfibre, because of its large surface area, not only responds more rapidly to heat, but utilizes lower molding temperature. This reduces the time required to heat or to cool the mold and makes possible rapid compression molding cycles. Because of the shrinkage inherent in the material, the pressure required to mold Polyfibre to full density may also be reduced. This makes it possible to build relatively cheap, lightweight molds, with cooling and heating channels close to the working surface. The end results are reduced molding time, greater production rates, the use of low-cost lightweight molds and lower molding pressures, while at the same time the original aim of increased molding speed with fibrous raw materials is achieved. Such procedures are designed to give a molding of full polystyrene density (1.05).

One of the outstanding properties resulting from compression molding of Polyfibre is improved toughness. Bulk polystyrene moldings are relatively brittle. Oriented Polyfibre has not only high tensile strength, but low brittleness. Even when Polyfibre moldings are carried to complete density, a large portion of the fiber's high impact strength is retained in the molding. Threefold increases in impact strength over that of bulk polystyrene moldings are not uncommon.

Until the advent of this new fiber, the low-pressure bag molding of thermoplastic materials had not been considered commercially feasible. Polyfibre's rapid absorption of heat based on its large surface area and its ability to shrink when heated have made possible its commercial use in low-pressure bag-molding fabrication. This greatly widens the scope of thermoplastic fabrication. First, large-size thermoplastic moldings can now be obtained with inexpensive equipment and low-cost molds without the use of high pressure. Second, complex contours, impractical in compression molding, become practical through bag molding. Third, and probably most important in its contribution to thermoplastic fabrication, is the

fact that molding densities can be accurately controlled. Molded Polyfibre densities ranging from 0.4 to 1.05 are entirely feasible.

As previously pointed out, the impact strength of Polyfibre is one of its outstanding characteristics. Retention of fiber orientation in the finished molding undoubtedly accounts for the impact-strength improvements over moldings made from bulk polystyrene. Even at full density (1.05), Polyfibre moldings usually show strength increases which indicate that some orientation still remains.

As density is decreased, the impact strength increases rapidly. Below a density of 0.70 the samples of the material bend over under impact and the results, although high, are unreliable. At 0.70 density, however, the impact strength of a 4 per cent solvent material is some nine times that of polystyrene. Solvent content effects are small, except as they are related through molding temperature to specific gravity. The modulus of elasticity, as calculated from flexural data, ranges from 0.3×10^5 at a specific gravity of 0.3 to 2.0×10^5 for a specific gravity of 1.0.

Polyfibre's hardness is related directly to specific gravity. Tests were made on the Rockwell Superficial Hardness Tester using a 15-kg. load on a ½-inch ball. Below 0.7 specific gravity, equipment which would give reliable results is not obtainable. As would be expected, press molded samples of a definite specific gravity give a slightly greater surface hardness than those made to the same density by bag molding. This is a result of the density gradient across the thickness of the sample and varies with the rate of transfer of heat into the sample during molding.

One property which is greatly affected by solvent content of the Polyfibre is that of heat distortion. At higher temperatures, the solvent acts as a plasticizer. Thus high solvent content results in a lower heat distortion temperature. Here the heat distortion is defined as that temperature at which 1 per cent shrinkage takes place when the sample (50 mm. square) is immersed in a water bath of controlled temperature for 10 min. Specific gravity appears to have little effect on the heat distortion temperatures of Polyfibre moldings.

Since these moldings are essentially combinations of air and polystyrene, it might be expected that they would show porosity.

Such is not the case. After immersion in water for 24 hr., Polyfibre, even in the lower densities, shows scarcely twice the water absorption of polystyrene at full density.

Distribution of density throughout a Polyfibre molding depends upon the molding cycle. For example, rapidly molded samples show high densities at the surfaces and low densities at the center. The use of one hot platen and one warm one shows a density gradient from high, adjacent to the hot platen, to low, adjacent to the warm one. This makes it possible to obtain a high variety of density gradients throughout Polyfibre moldings.

To recapitulate:

1. Low-pressure bag molding of large thermoplastic polystyrene parts is now practical.
2. Inexpensive molding equipment may be used.
3. Large moldings of controlled specific gravity ranging up to 1.05 may be made.
4. Controlled specific gravity gradients throughout the molding are now possible.
5. Improved impact strengths may be obtained.
6. New low dielectric constants are possible.
7. Directional strength properties may be controlled.

FORTISAN

This yarn, developed by Celanese Corporation of America in association with British Celanese, Limited, has been going into numerous war applications. It is of interest because of its strength, resistance to stretch, durability and dimensional stability. It is adapted not only to textiles but also to laminating.

Fortisan is a regenerated cellulose type of yarn, the structure of which is highly orientated and its micelles firmly bonded together. It is producible either as continuous filament or staple yarn. It has a wide range of deniers and deniers per filament. Currently deniers of 30 and upwards are produced at about 0.7 denier per filament. Much finer deniers have been made and filaments down to 0.1 and less have been prepared.

Up until comparatively recently Fortisan had the following physical properties:

	Dry	Wet
Tenacity..............	5.6 gr per denier	4.0
Elongation, %..........	6.0–6.5	6.0–6.5
	RH 65% at 70°F	

Much higher strengths, however, had been obtained in the laboratories, and currently a special high-tenacity Fortisan having the following properties is being produced:

Tenacity, dry...............	Over 7.0 per denier gr
Tenacity, wet................	Over 6.0 gr per denier
Elongation, %, wet or dry.....	6.0–6.5
RH 65% at 70°F	
Modulus of elasticity in tension at 65% RH.................	4.5 million

An idea of the unusually high strength of Fortisan may be realized by comparing it with metals.

	Ultimate Strength psi	*Spec Gravity (to 0.1)*	*Strength ÷ Sp gr*
High tenacity Fortisan..........	138,000	1.5	92,000
Iron wire (unannealed)...........	60,000	7.5	8,000
Steel....................	80,000–330,000	7.7–7.9	10,400–42,300

Even higher strengths have been obtained and are planned for future production. No definite limit of ultimate possible strength of Fortisan is yet in sight. At the present time it is being used in applications where extreme strength, lightness in weight, or both are required.

Because of its unusual properties, it is believed that it will find many applications after the war.

STRONG RAYON YARN

A new high strength viscose rayon yarn designated for experimental purposes as Fiber G has been developed by the Rayon Division of E. I. du Pont de Nemours and Company, Inc. It is claimed that the yarn, a result of the adaptation of a new spinning method, has a tensile strength of 5 g. per denier dry and retains 75 per cent of its strength when wet. Thus the wet strength of Fiber G is about the same as the dry strength of the high tenacity viscose rayon tire yarns. A low elongation of only 6 to 7 per cent is reported. The ex-

perimental sizes are 240 denier with 120 filaments and 1100 denier containing 480 filaments.

In view of the superior wet strength of the new yarn, it is expected that it will find widest usage in the field of industrial textiles. But it may prove useful in the apparel field for such articles as bathing suits, shoes and corset nets. It may also supplement or replace certain types of yarn now used for military purposes.

AVISCO STAPLE FIBER

The American Viscose Corporation is now producing on a commercial basis its Avisco (extra-strength) viscose process rayon staple denier. The new staple is available in standard lengths suitable for the different spinning systems. It produces finer counts than standard staple fiber and it also has greater strength. It can be spun as fine as 200/1 and 300/1 cotton numbering system, a size finer than that usually spun of the longest length cotton staples by American mills. The introductory price was $0.26 per lb.

Commercial applications reported include flat knit fabrics, simplex glove fabrics, tricot knit dress goods, fine broadcloths, foundation fabrics, sheer handkerchief, dress and shirt materials.

SOYBEAN FIBER

Soybean fiber was first developed by the Ford Motor Company and by the end of 1942 output had reached 1000 lb. per day. It was planned to step up production to 5000 lb. per day in a new plant which, however, was not built because of war conditions.

Commercial production of the new soybean fiber started in Cincinnati, December 2, 1943, in the new plant.

Soybean fiber is one of the first non-animal protein fibers to achieve commercial importance. In appearance, it is a loose, fluffy mass and looks like scoured wool. Its color varies from a light tan to white. It has a medium luster between that of wool and mohair and has a rather warm, soft feel, a natural crimp, and a high degree of resiliency. It is not so strong as wool but in the laboratory batches of it have been experimentally produced which are even stronger than wool.

The important steps in soybean fiber manufacture are as follows: The oil is extracted from the soybean through the use of a solvent and the residue is a soybean meal. The protein is removed from this meal by treating it with a weak alkaline solution, such as 0.1 per cent sodium sulfite. The resulting solution is then clarified by either filtering or centrifuging. The protein in the curd is then precipitated by an acid and the resulting curd is washed and dried.

To clarify, the precipitation must be carried out at just the right temperature and *p*H in order to get a curd that can be handled properly during the subsequent washing and drying.

Once the protein is removed from the meal, it is dissolved to produce a viscous solution of about the same consistency as molasses. This solution must be carefully controlled. It must have a high solids content, which is difficult to get because proteins in high concentrations tend to form a gel. Yet, with careful control, it is possible to produce solutions with as much as 20 per cent protein.

The solution itself must then be aged before the required viscosity and stringiness are reached.

The aged solution is forced through spinnerets into an acid precipitating bath and the resulting filaments are collected from this bath on bobbins or reels. Filaments must be stretched as they are collected. This is done by pulling them through the acid bath and over two glass pulleys, one of which revolves faster than the other to exert the desired stretching effect.

The fiber is then set by immersion in a formaldehyde bath and is dried under controlled humidity and temperature, after which it is cut into desired lengths and is ready for shipment.

FINENESS MEASUREMENTS

Types	*Old, 1939*	*New, 1944*
No. of fibers	200	400
10–20 microns	1%	12%
20–30 microns	97%	84.25%
30–40 microns	2%	3.5%
Over 40 microns		0.25%
Average microns	26.81	23.18
Standard deviation	2.04	3.63
Coefficient of variation	7.61	15.65

It is interesting to note that the coefficient of variation which reflects the uniformity of the fibers is twice as high in the new product, approaching the variation in wool fibers, which run from 19 to 25 per cent. The staple length is approximately 2 in.

The tensile strength, compared with wool of the same grade, gave the following results:

TENSILE STRENGTH AT 70°F

	Soybean Staple, 1944 *psi*	*Wool Top, 62s* *psi*
Dry	11,450	21,000
Wet	4,240	17,700
Strength loss from dry	63%	15.8%

In the dry state the soybean fiber is approximately 45 per cent weaker than a corresponding grade of wool and 76 per cent weaker in the wet state.

In the conditioning oven where the fiber was exposed to 220°F., a considerable yellowing takes place, indicating that the fiber is not able to stand a high temperature. This same yellowing was observed on other protein fibers such as Aralac and Lanital.

Chemical Properties. The fiber is strongly on the acid side, which is indicated by the *p*H of 2.7.

SWELLING CHARACTERISTICS OF FIBER

Types	*1939* *Microns*	*1944* *Microns*
Glycerin	26.6	23.2
Water	32.8	27.5
n/10 Caustic soda	43.6	31.3
Swelling	%	%
Water	23	18.7
Caustic soda	63.5	35.1

In this respect the fiber is now about equal to Aralac fibers (casein protein).

The fiber resists carbonizing with 4 per cent sulfuric acid, but turns yellow. In the acid condition, it is quite harsh and brittle and

through neutralizing the original softness is only partly restored. The fiber shows a high affinity to acid and chrome colors, but when dyed at *p*H's below 3, the fiber becomes very harsh and brittle. At the *p*H of 7 the fiber dyes very strongly red with Benzopurpurine. This shade is considerably deeper than that obtained on Aralac fibers at the same *p*H.

Soybean fiber is still admittedly in the development stage and it is as yet too early to say definitely just what its part will be in the textile world. It is emphasized that it should not be viewed as a substitute for wool, cotton, rayon or any other fiber, but that it represents an entirely new raw material with virtues of its own. Research on it is still under way and it has undergone improvements in some of its properties, such as, for example, the resistance to alkalies. It is said to be suitable for blending with rayon and cotton. The material is of particular interest, as it offers another new outlet for farm products.

CHAPTER VI

New Adhesives

Many believe that the era 1940 to 1960 will be noted for progress in the construction of homes, household appliances and other structures, just as there was progress in 1860 to 1880 in civil engineering, in 1880 to 1900 in mechanical engineering, in 1900 to 1920 in electrical engineering and in 1920 to 1940 in chemical engineering.

Great strides have been made during the war in fabrication, the expansion in productive capacity for various materials including the light metals and plastics, and finally the striking developments in adhesives which have made it possible to combine basic materials of various kinds into new finished products.

Engineers have long wanted new adhesives that will permit the bonding of metal, wood, glass, ceramics, plastics, fibers and rubber in any desired combination. A possible answer to this problem has been found in Reanite and Cycleweld cements, thermosetting plastics that are applied to the surfaces of the units to be bonded and then cured under heat and pressure. This process is said to form structures stronger, lighter and cheaper than those joined by welding, riveting and other conventional methods.

The basic formulation of Reanite and Cycleweld adhesives has not been officially released, but it is reported that they are both combinations of various rubbers and thermosetting resins.

REANITE

One of the basic patents on Reanite No. 2,311,656 dated February 23, 1943, contains the following comment on the composition of this new adhesive:

The improved rubber derivatives of this invention are prepared by milling sulfur or equivalent rubber vulcanizing agents, such as selenium, vulcanizing types of accelerators, etc., and one or more suitable conversion reagents, into rubber,

such as Hevea smoked sheet, or pale crepe, sheeting the product out to relatively thin sheets, heating the sheets under suitable conditions until the desired reaction takes place, and then masticating the product to render it soluble in rubber solvents. To obtain the improved rubber derivative of this invention the sulfur must be chemically combined in the resulting rubber derivative in rather definite proportions. Suitable rubber accelerators may be added to the mixture if desired.

Early development work on Reanite was conducted by Dr. H. J. Reaney in collaboration with the Canadian National Resource Council. The Reanite Company, along with their series of U. S. A. and foreign patents, was later purchased by interests connected with the U. S. Stoneware Company. The Reanite Company of U. S. A. is owned jointly by the General Tire and Rubber Company and Chamberlain Engineering (Canada) Ltd., the latter being the Canadian affiliate of the U. S. Stoneware Company.

The Reanite bonding process results in a bond that gives remarkable adhesion not only between related materials, but also between materials of an entirely dissimilar nature. It is suitable for use with almost all metals, natural or synthetic rubber, plastics, wood, leather, glass and ceramic materials, and it provides a more effective, less expensive method of material fabrication.

The Reanite bonding process develops an adhesion strength between rubber and metal up to 1200 lb. per sq. in. in tension, depending upon the rubber compound and the nature of the metal to which it is bonded. Standard tests for conventional rubber-to-metal commercial applications call for a bond 250 to 300 lb. per sq. in. which has been considered normal for most processes.

Rubber may be bonded by the Reanite process to virtually all metals: iron, steel, stainless steel, brass, bronze, aluminum alloys, magnesium and its alloys and copper. It is not necessary to brass-plate the metal first.

Stronger bonds are normally obtained when the rubber is applied in an uncured state, but excellent bonds are usually obtained with previously vulcanized rubber. Rubber stocks containing large quantities of clay, reclaim, etc., give adhesion according to their physical properties.

Excellent bonds have been obtained with Thiokol and Neoprene, and reasonably satisfactory bonds with Hycar and Buna S com-

pounds, but only poor adhesions have been achieved with Butyl rubber, and with rubberlike materials such as Tygon and Koroseal.

Metal-to-metal bonds by the Reanite process as high as 3000 lb. per sq. in. in shear strength have been attained. Assembly may be metal-to-metal direct, or with a thin layer of rubber between. The latter method is of particular advantage where vibration fatigue may be severe or sound insulation is desirable.

In repeated tests between Reanite and riveted and spot-welded joints, the Reanite joint not only proved stronger but also had greater impact strength. Creep resistance was definitely better than with most riveted construction. The process is said to be of particular advantage in applications where thin metal sheets must be solidly joined to heavy structural supports. Welding processes usually burn the thinner sheet, creating an unsuitable bond. Riveting, as generally used, provides comparatively small contact area and relatively poor fatigue resistance. The Reanite process, however, forms a continuous bond between the thin metal sheet and the heavy reinforcing member — giving substantially the rigidness and strength of a welded joint but with added fatigue resistance and definite sound-insulation values.

Excellent adhesions have been obtained with certain plastics of the phenolic group and with other thermosetting plastics. Experimental work with plastics is not completed, but it may be possible to obtain satisfactory adhesions with most of the better known plastics.

Reanite will bond wood to steel, aluminum, copper and other metals with a bond stronger than the wood itself. The process makes possible the bonding of thin metal sheets or foils to plywood with almost integral adhesion. Metal-bonded plywood becomes an entirely new material of construction.

APPLYING THE ADHESIVE. The Reanite bonding process is simple. Only one cement is used, and one coat is usually sufficient to secure good adhesions, though a second coat may be applied if thicker films are desired.

Reanite cement is applied to two surfaces to be joined by spray, brush or dipping. Metal-to-metal application may be made with Reanite tape, a thin tape that comes in various widths and is laid

between the surfaces to be joined. Liquid Reanite is permitted to dry for an hour or longer. After drying, the surfaces to be joined are pressed together with the application of mild heat and pressure. The pressure need only be enough to hold the surfaces in intimate contact over their entire area and to permit the adhesive to flow as heat is applied. With perfectly flat and well-prepared surfaces, the

Courtesy U. S. Stoneware Co.

FIG. 23. Reanite cement may be applied by brush as shown.

pressure need be no greater than that of an ordinary electric household iron. Curing may be by steam, hot air, hot plates, ovens or electronic heating. Curing times vary from 15 min. to 2 hr. Stronger bonds are obtained when the bonded assembly is permitted to cool naturally, though water quenching can be employed where quick cooling is necessary.

No weakening of the bond has been observed at temperatures extending from 0° to 200°F. Between 200° and 300°F., and between 0° and −50°F., the bond shows only slight loss of strength. Even at

these temperature extremes, however, it is stronger than the bonds developed by most processes at room temperatures.

An independent laboratory, in reporting its observations on tests of low-temperature bonds, states: "The samples (aluminum bonded to aluminum) failed to break at the capacity of the machine at temperatures as low as $-40°F$. It is definitely established that adhesions at least as much as 880 lb. per sq. in. can be obtained at this low temperature. Using the conventional method of test with our buttons, adhesions as high as 1000 lb. per sq. in. were obtained at all temperatures tried up to 200°F."

One of the important advantages of Reanite is its complete freedom from any tendency to attack metal or other surfaces. Examination of test samples after periods as long as one year disclosed no signs of corrosive attack. Not only is it noncorrosive to metals, but it is said to possess excellent corrosive resistance in itself, being unaffected by any of the chemicals to which rubber is resistant. It is entirely unaffected by fresh or salt water, and test samples have been immersed in both fresh and salt water for as long as three months with no noticeable effect. The bond is apparently permanent and shows no weakening with age.

CYCLEWELD ADHESIVES

Cycleweld is a rubber derivative like Reanite and is believed to be quite similar in composition. No information has been released on the composition of Cycleweld adhesive, but much publicity has been given out in connection with its applications in war work.

The principle of Cyclewelding was developed before the war by Chrysler Corporation. In 1938, interior insulation material was attached to car roofs by this adhesive cement. By 1940, the cement had been so improved that Cyclewelded bonds were holding together many passenger car parts, including panes of glass, trunk covers, cowling ventilators and parts of fenders.

In early 1941, while automobile uses for Cycleweld were being rapidly expanded, Chrysler with Army Air Forces at Wright Field, Dayton, Ohio, began the first experiments in applying Cycleweld to the aircraft industry. The strength of Cyclewelded joints was increased more than 100 per cent.

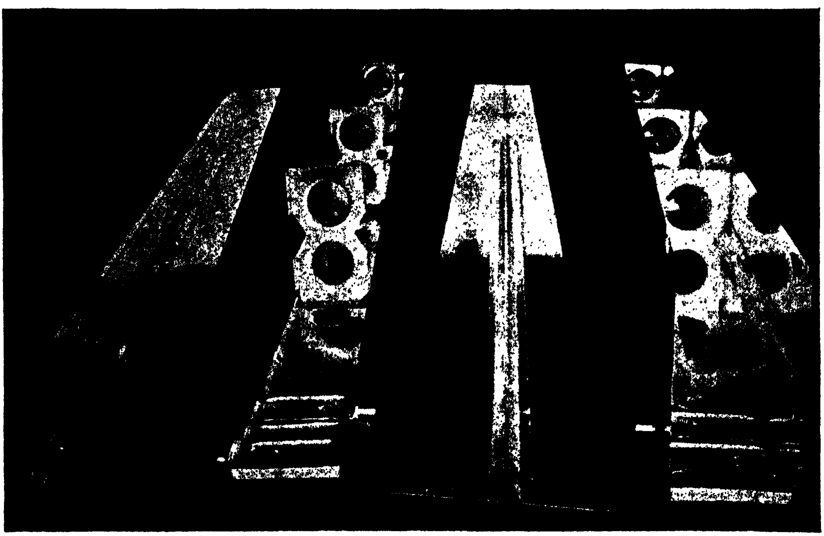
In August, 1941, Chrysler Corporation made arrangements with the Goodyear Tire and Rubber Company of Akron, Ohio, to aid it in producing cement, and Goodyear now does some of the preliminary production work on Cycleweld cement before the final processing by Chrysler Corporation.

Since 1941, the strength of Cycleweld cement has been further substantially increased.

The Cyclewelding process was first described by Chrysler in October, 1942.

The process has been accepted by both the U. S. Army and Navy Air Forces for structural and nonstructural parts for which it is suitable and has had widespread use in the aircraft industry.

As in the case of Reanite, Cycleweld adhesive is simple to apply. The cement can be brushed on the surfaces to be joined or laid on



Courtesy Chrysler Corp.

FIG. 24. This shows aluminum aircraft sections bonded by Cyclewelding.

in the form of a tape. Heat and pressure are then applied to the joint. The process can be used to unite metal to metal, metal to wood, metal to rubber and metal to plastics so that the joints will be stronger, easier to build and cheaper than those riveted or welded.

Among the aircraft applications have been Cyclewelded wing flaps for fast fighter planes, ski pedestals for gliders, essential structural sections for medium bombers, fiber and wooden gasoline tanks and hundreds of other aircraft parts. Experiments are being conducted on completely Cyclewelded airplanes and gliders designed specifically to use this new method of bonding.

In tests comparing Cyclewelded and riveted metal joints, the shear strength of the Cyclewelded joint is almost twice that of the riveted joint, its impact strength many times greater and its creep strength at least 50 per cent greater. Especially significant is the fact that no Cyclewelded joint has ever been broken by vibration. On all the tests the metal itself, away from the joint, has broken before the joint is separated.

Cyclewelded parts are reported to be better than those riveted or spot welded and also less costly to make. Chrysler Corporation reports that 90 per cent in cost as compared with riveting in addition to considerable manufacturing time is saved on one part. The same is true in a greater or lesser degree of other parts that can be Cyclewelded.

Chrysler Corporation also reports that, on a stabilizer it built by using the Cycleweld process, the number of rivets was reduced from 5500 to about 30 and strength and rigidity were increased.

The process is particularly adapted to wood-constructed aircraft, and is said to be the lightest and strongest method of attaching wood to metal. In most instances, it has produced joints far stronger per square inch than bolted joints. On an experimental wooden airplane, nuts and bolts on the most important beam fittings were practically eliminated with a saving of several hundred pounds in weight.

A significant use for Cycleweld is sealing of sheet rubber around the cabins of high-flying airships. It has proved to be just as strong for bonding rubber to metal as it is for metal to metal.

Chrysler started with one cement and one process, but now has developed varieties that have extended the scope of Cyclewelding. The three general processes include (1) the original Cyclewelding method, utilizing higher degrees of heat and pressure, (2) Cycle bonding with low temperature and medium pressure to effect the

bond, (3) Cycle bonding with low pressure and medium temperature.

Postwar Applications. The development of new stronger adhesives, such as Reanite and Cycleweld, will open up a vast field of postwar applications to the use of entirely new materials. One such new material is metal-bonded plywood, which combines the beauty of stainless steel or aluminum with the light weight, heat-insulating and sound-deadening characteristics of plywood, a material that may be used in prefabricated housing, kitchens, assemblies, furniture, refrigerators, boats, automobiles, airplanes and many other structures.

The new adhesives make it possible to combine all kinds of basically different structural materials so that the particular advantages of each type may be fully utilized. For example, thin sections of metals may be used to impart strength, while plywood, plastics, glass or other decorative materials might be utilized for beauty or other special characteristics. The possibilities are almost limitless. As one of the originators of a new adhesive has expressed it, "The ideal structure has not yet been built."

FURFURAL RESIN ADHESIVES

The use of furfural resin adhesives in the aircraft industry represents the first commercial development of plastics materials purely from furfural derivatives. The unusual characteristics of furfural resins have been under investigation at the Plastics Industries Technical Institute, Los Angeles, Cal., for several years. Various types of coatings, molded, laminated and impregnated assemblies have been prepared experimentally. Recent emphasis, however, has been on adhesives because of growing demands from the aircraft industry, and furfural resin adhesives are now being produced in a small pilot plant.

Furfural ($C_4H_3O{\cdot}CHO$), an aldehyde, produced commercially on a large scale from waste vegetable products, has long been regarded as a useful solvent, as have its derivatives, furfural alcohol, tetrahydrofurfural alcohol and hydrofuramide. In the plastics industry, it is best known in combination with phenol, and the pure furfural resins are similar to phenol-formaldehyde in behavior.

The new furane resins are distinctly thermosetting in character, although thermoplastic derivatives are available.

Furfural resin adhesives are being produced in two grades — one for hot setting, and the other for room-temperature setting. They are described as follows by John Delmonte, Technical Director of Plastics Industries Technical Institute.

a. Resin XV (High-temperature Setting) — designed largely for metal products and as pretreatments for some special plastics.
b. Resin X (Low-temperature Setting) — applied largely to plastics products.

Room-temperature setting adhesives are important in the aircraft industry because no special heating apparatus is required and cemented pieces may be prepared at ordinary temperature. Low-temperature setting is particularly useful when the materials being bonded together are affected by heat, as are plastics and wood products, which may warp or deform if localized high temperatures are required. The warpage may be due to uneven expansion coefficients or uneven moisture distribution in wood products.

One drawback of many resin adhesives has been the presence of volatile matter — either water or solvents — which serves as a vehicle for the resin. In wood laminates, the moisture content of the veneers is unbalanced, and warpage or stresses may develop. When relatively nonporous materials, such as laminated plastics or metals, are being joined, however, the diffusion of volatile matter outside the glue line is a slow process, and strength of the joint suffers accordingly. Most adhesives cannot exhibit their best strength so long as volatiles are present. Many adhesives are therefore applied first to the surfaces, and some of the volatile matter is allowed to evaporate before they are pressed together. When the surface becomes tacky, which is indicative of the retention of a residual amount of solvent, the surfaces are pressed together. In contrast, the furfural resin technique does not wait for a tacky condition, and surfaces are placed together any time after glue is applied.

Resin X adhesive contains no volatiles, but Resin XV contains

approximately 50 per cent volatile matter. The 100 per cent solids Resin X adhesive is a liquid thermosetting resin that has been stabilized for indefinite storage. To activate for application it is mixed with a small amount of catalyst which will enable the resin to cure at room temperatures (above 75°F.). A batch of the adhesive may be prepared and cast into a sheet form just like any other cast-plastic material because it contains no volatile matter. Physical characteristics of this adhesive fully cured are as follows:

(Tests by ASTM Standards)

Compression strength	12,000 psi
Ultimate tensile strength	4,000 psi
Modulus of elasticity (flexure)	1,100,000 psi
Shear strength (Johnson shear tool)	5,700 psi
Flexural strength	9,000 psi
Water absorption (24 hr)	0.05%

These properties are characteristic of the adhesive itself at the glue line, though other test data are for the combination of the Resin X adhesive with other materials.

RESIN X BONDED PHENOLIC LAMINATES. Most experimental work has been in the application of Resin X adhesive to laminated phenolics, paper or canvas base. This adhesive, when properly applied and cured, should result in a 100 per cent failure in the laminated phenolic. In a typical case, the entire phenolic skin was pulled away at the time of failure. During shear tests, the phenolic laminate delaminated. This adhesion is explained in part by affinity of the reactive Resin X adhesive for phenol-formaldehyde resins. The test was the three-block shear method whereby test specimens were formed by three blocks measuring 1¼ in. by 1¼ in. The center block projected ¼ in. above the others and the shear load was shared by two glue lines.

Various tests were performed after cure temperatures of 85° and 122°F. to ascertain the influence of time and temperature on cure of the adhesive, as manifested by its shear strength between laminated-phenolics canvas base. Although these data are applicable particularly to laminated phenolics, they also indicate the rate of cure of the cold-setting adhesives. A maximum shear strength is

indicated by this method of test, in the neighborhood of 3500 lb. per sq. in., where the phenolic laminate failed completely. The tests were all performed at the prevailing room temperatures of 75° to 80°F., and loading was applied on a Tinius Olsen Universal Tester at a crosshead speed of 0.2 in. per min. The laminated phenolic pieces were ¼ in. thick. In curing these pieces, no pressure was used, and the surfaces of the laminated phenolics were not sanded or roughened.

In general, phenolic laminates may be soundly bonded together with Resin X adhesive, overnight at 120°F. or after several days at temperatures of 85°F. Some experiments at 70°F. or lower, however, show that cure may be retarded considerably longer with different catalysts.

The strength of the Resin X adhesive was also evaluated at temperatures from 20° to 175°F. in the bonding of laminated phenolics. There is a decided dropoff in values at higher temperatures. Within the range tested, the failures occurred in the laminated phenolics in all cases.

As may be expected in an adhesive containing no volatile matter, glue-line thickness should not be critical. This is borne out by data on a test of the shear strength of fully cured pieces of bonded laminated phenolics for different thicknesses of glue line. The thickness of the glue line was adjusted by spacers placed at the edges of the test specimens. Slightly higher shear strength was exhibited at the thicker glue line (1/32 in. thick). The noncritical nature of the glue-line thickness of Resin X adhesive makes possible a technique of casting-gluing, whereby rough or porous surfaces may be joined simply by pouring sufficient Resin X adhesive between them to fill the voids. This can be demonstrated readily by bonding laminated phenolic to a porous firebrick.

Among experimental aircraft applications of Resin X adhesives are cemented ammunition boxes and floorings. In addition to phenolic laminates, Resin X adhesive works quite satisfactorily with MR laminates and reasonably well with Laminac, after it has been given a special surface treatment. Compreg is also bonded satisfactorily, though it requires slight sanding on the surface.

RESIN X BONDED RUBBER. Resin X adhesive has been successfully applied to natural rubber, Neoprene, Perbunan, Buna S and Thiokol, with zero or low pressures and low temperatures. There is, however, an important difference in applying Resin X to rubber goods as compared with plastics. The rubber is first treated with concentrated sulfuric acid, followed by washing in water. In this manner, bonds are produced which give rubber failure in tension or shear. This has been observed in bonds of rubber to polymethyl methacrylate, laminated phenolic, and 24 ST aluminum alloy with Resin X adhesive. Again, glue-line thicknesses are not critical, and curing temperatures are employed.

RESIN X BONDED WOOD. Resin X adhesive has shown particularly valuable properties when applied as a cold-setting or hot-setting adhesive to wood. The absence of water or alcohol tends to give a product that has little tendency to warp. Experiments upon curved plywood sections demonstrate a much greater stability of shape with Resin X adhesive compared with other cold-setting adhesives employing water or alcohol.

The good penetrating qualities of Resin X adhesive may be employed to develop a fully impregnated wood structure at the time of laminating by applying sufficient adhesive solids at the glue line.

When gluing takes place over a long period of time, it is best to chill the Resin X adhesive before adding catalyst, and then keep it cool. In this manner pot life is extended several hours, often a desirable procedure in gluing up wooden structural members. Otherwise the pot life of Resin X adhesive is short because of the active nature of the resin.

Among the interesting properties of Resin X adhesive as a cold-setting plywood adhesive is its resistance to boiling water. The 3-hr. boiling-water test outlined in AN-NN-P-511B (Army Navy Aircraft Plywood Specification) is readily withstood, with wood failure occurring for the strip shear tests. Various strip shear tests for different glue spreads are tabulated in Table II. These tests were performed in accordance with the AN Specification just cited and cover the properties of Resin X as a cold-setting adhesive.

The glue spreads may be applied heavily because there are no

TABLE II

Strip Shear Tests on 1/16 in. 3-ply Vertical Grain Birch
Resin X — Cold Set Adhesive — 16 g/sq ft

	psi	Dry Shear % Wood Failure	Aver	psi	Wet Shear % Wood Failure	Aver
1	450	95		324	100	
2	414	90		324	95	
3	416	100	415 psi	316	100	319 psi
4	380	100		314	100	
5	411	100		318	100	

volatiles. Since it is a good penetrating adhesive, there is an advantage in penetrating into and helping to stabilize the wood.

Resin XV Bonded Metals. In bonding aluminum and brass, best results have been obtained in applying hot-setting Resin XV. This is true for any bond of plastic or wood to the metal. Experiments in applications to metal are still in their early stage, but some exceptional results have already been observed in the laboratory. For example, two aluminum blocks bonded together with Resin XV exhibited tensile strengths in excess of 3500 lb. per sq. in. before the blocks separated, a remarkably high figure compared with other adhesives.

Other Forms of Resin X. Although this discussion has dealt primarily with Resin X in its adhesive form, there are other promising uses for the material. Molded, laminated, casting grades, surface coatings, impregnating agents, etc., have been prepared from these resins. An impregnating agent for plaster of Paris and an air-drying thermosetting surface coating are of interest to the aircraft industry.

Dry plaster of Paris will readily absorb up to 50 per cent Resin X impregnating agent. When cured under the specified conditions, the compression strength of the plaster is increased approximately 400 per cent and flexural strength approximately 700 per cent and the plaster of Paris is rendered more waterproof. Resin X will penetrate a thickness of several inches in dry plaster. Although the improvement in physical properties does not bring the plaster up to

the range of cast-phenolic resins, the impregnated plaster does have an advantage in better dimensional stability and freedom from shrinkage. At the same time, the plaster becomes hard and more chipproof and can readily be polished to a high luster.

In applying Resin X impregnating agent to plaster of Paris, the usual technique of preparing the plaster of Paris form block or die is followed. When the shape is correct and the plaster dried, Resin X is brushed or the piece is dipped into the resin, which rapidly diffuses through the pores in the plaster of Paris. This technique will undoubtedly find application to various jigs and tools, permitting plaster of Paris forms to handle greater stresses.

The resin-impregnated plaster must be heated to effect the cure. At least 18 to 20 hr. at 200° to 220°F. are necessary to realize full strength. Still further strength can be obtained by a second impregnation and cure period. This technique should greatly extend the usefulness of plaster of Paris.

Resin X developments, though under investigation in the laboratory for several years, are still in their infancy. They show promise, however, of taking their place in the plastics picture along with other thermosetting materials. Raw materials for their manufacture are abundant, and interest in the resins developed at Plastics Institute will undoubtedly continue to grow.

DU PONT'S NO. 4624 THERMOPLASTIC–THERMOSETTING ADHESIVE

No. 4624 thermoplastic-thermosetting adhesive, a new adhesive which may be classified as a modified polyvinyl material, was described by E. I. du Pont de Nemours & Company, Inc., in a bulletin dated March 1, 1944. It is recommended by the du Pont Company for laminating wood to wood and is advantageous in the manufacture of molded plywood. A large plywood manufacturer has found the new adhesive satisfactory in extensive use within the past year.

No. 4624 has shown the following advantages as compared with phenol-formaldehyde adhesives:

1. *Less sensitivity to moisture variations in wood.* No. 4624 adhesive will tolerate from 3 to 18 per cent wood moisture. With the

usual phenol-formaldehyde adhesive, the moisture content of the wood should be controlled between 5 and 12 per cent. Because wood is much tougher and more flexible at the higher moisture contents, it splits and cracks less when it is molded, and the veneer can be bent and laid around the forms with greater ease. It is probably not practical to control the moisture content of thin veneer definitely between 5 and 12 per cent during handling and fabrication except by air conditioning the workroom. The new adhesive is reported to be more foolproof than phenolic adhesives.

2. *Slip during molding.* When the 4624 film is first heated in the autoclave, it is thermoplastic and becomes fluid, thus permitting the layers of veneer to slip together into intimate contact. The film then thermosets and becomes nonthermoplastic. Thus, even if the plies are not initially laid in intimate contact (although this should be possible with wood containing 15 per cent moisture), or if the form is distorted under the autoclave pressure, there will be fewer open joints and hence less rejects. Again 4624 adhesive is more foolproof than phenolic adhesives. Users report that the initial thermoplasticity so reduces rejects in the bag-molding process that they find it more economical than phenolics in spite of its higher glue-line cost. The glue line is probably less than 5 per cent of the total cost of manufacturing molded plywood, and labor used in shaping and laying the plywood is lost when a part is rejected because of poor glue contact.
3. *Assembly time up to twelve months.* The adhesive can be applied in an ordinary glue spreader and may be assembled as soon as the solvents have evaporated (approximately 2 hr.). Immediate assembly is not necessary, however, because the coated strips may be stored for as long as 12 months before lamination. This is particularly advantageous with large or complicated assemblies, which may be in the process of fabrication for several weeks before being put in the autoclave where the glue lines are activated under pressure. The open assembly time of phenol-formaldehyde adhesives is at best only a few days, and any delay in completing the laying of the veneer or

in getting the fabricated part into the autoclave will therefore result in unsatisfactory activation of the glue line and hence a defective part.

4. *Flexibility of glue line after thermosetting.* The flexibility of the 4624 glue line means that, when the joint is loaded, the strain is well distributed over all contact surfaces resulting in dry shear strengths consistently higher than with phenol-formaldehyde and other less flexible adhesives. (Wet wood is itself flexible and so able to adjust itself to brittle glue lines. Therefore, the *wet* shear strength is not improved by the flexibility of 4624 adhesive.) Again the new adhesive offers a larger factor of safety than do phenol-formaldehyde adhesives.
5. *Low weight per square foot of glue line.* In one application 23 per cent less weight of dry 4624 film per thousand square feet of glue line is used as compared with a phenol-formaldehyde adhesive. This saving in weight is an important advantage in aircraft construction and in the design of portable military equipment.
6. Plywood manufactured with 4624 adhesive according to recommendations fully meets joint Army-Navy Specifications AN-NN-P-511B and AN-P-43.
7. No cases of dermatitis or "glue itch," resulting from the use of 4624 adhesive, have been reported, but there is no proof that no one is allergic to it.

The following directions for using 4624 adhesive will result in the highest quality plywood complying without deviation to joint Army-Navy Specifications AN-NN-P-511B and AN-P-43. Lower glue spreads will obviously reduce the cost of the glue line and may be satisfactory for many uses.

The adhesive is supplied in liquid form, ready to apply, at 20 per cent solids. No catalyst or thinner is necessary. It should be brushed or applied with a glue spreader on hard and medium density woods at the rate of 20 to 25 lb. of liquid adhesive per coat per 1000 sq. ft. of surface. Both contact surfaces should be coated twice. The coating should air dry a minimum of 2 hr. before assembly and bonding. Assembly and bonding up to 12 months after coating are

permissible. The glue line should be raised to a temperature of 275°F. (135°C.) and held for 20 to 25 min. of curing. No cooling is necessary after curing of the glue line.

A typical bag-molding procedure for preparing a three-ply structure from 1/16-in. veneer would be to heat for 10 min. to allow heat penetration under approximately 40 lb. per sq. in. steam pressure at 275°F. (135°C.). The adhesive is cured for an additional 20 to 25 min. at a temperature of 275°F. It can also be used in the hot-plate press bonding procedure using the conventional pressures, for various woods. In this type of bonding, however, plywood manufacturers have been accustomed to using a lower priced type of adhesive that does a fairly satisfactory job. This type of bonding does not require the quality of initial thermoplasticity found in 4624.

The adhesive can be activated by high-frequency radio (electrostatic heating), a process that is finding some uses in the plywood industry.

The adhesive weighs 7.68 lb. per gal. and contains 20 per cent solids, i.e., 1 gal. of 4624 adhesive will deposit 1.536 lb. of glue line. It should be applied as received, although, if solvents have evaporated from the solution, it may be thinned to its original consistency.

No. 4626 adhesive is an analog of 4624 adhesive containing slower evaporating solvents and No. 4647 adhesive is an analog of 4624 adhesive containing faster evaporating solvents.

These slower drying solvents are used to prevent the curling of plywood during the evaporation of the adhesive's solvents. But No. 4624 is satisfactory in this respect for most uses.

Ponsolve, or denatured alcohol, may be used to thin 4624 adhesive and to wash equipment. Inclusion of 20 per cent water in the solvent will slightly improve its cutting action. The adhesive should be promptly removed from glue spreaders and other equipment, for the dried film is difficult to dissolve.

OTHER NEW ADHESIVES

The foregoing adhesives should not by any means be considered as representing all the new adhesives that have been developed or even as necessarily the most important ones. Various other adhe-

COMPARISON OF ADHESIVES

Adhesive	Form Supplied	How Prepared for Use	Life of Mixed Adhesive	Pounds of Dry Adhesive per 1000 sq ft Glue Line	Approximate Cost of 1000 sq ft Glue Line	Assembly Time	Time and Temperature for Lamination	Moisture Allowable in Wood	Dry Shear Strength*	Wet Shear Strength*	
										3 hr Boil	48 hr Soak
4624 (du Pont) (polyvinyl)	Solution in mixture of alcohols and water	Use as received	12 months or more	16–20 Molded	$27 for molded plywood. Less for flat	6 months	25 min at 275°F	3–18%	563	445	
Phenol Formaldehyde	Dry, in solution or as impregnated paper	Solid resin dissolved in denatured alcohol and water. Solution and paper used as rec'd	Several weeks for solution. Impregnated paper should be refrigerated	12–18 Flat 18–28 Molded	$4 for flat plywood, $6 to $8 for molded.	1 week	6 min at 275°F	5–12%	441	426	
Urea Formaldehyde	Dry powder or in solution	Solid resin dissolved in water. Accelerator added	8 hr	20–25	$4 to $5 for flat	1 hr	8 hr at 75°F	2–15%	433	0	403
Blood Albumen†	Powder or flake	Dissolved in water	Several days	10–30	$2.70 for flat	40 min	16 hr at 75°F.	2–5%	584	413	
Soya bean Protein	Powder or "flour"	Dissolved in water	4 hr	10–15	$1.00 for flat	10–15 min	3 min at 230°F	5–15%	485		0
Casein	Powder	Dissolved in water. Preservatives and accelerator added	12 hr	20–25	$5 to $6 for flat	15 min	16 hr at 75°F	2–5%	500		292
Starch	Powder or "flour"	Dissolved in water and alkali	Several days	15–20	$1.00 for flat	20 min	16 hr at 75°F	2–5%	415	0	0

* Pounds per square inch (psi)

† Subject to fungus, stains

sives have been developed which cannot be publicized because of military restrictions. It is understood, for example, that one of the most promising new adhesives is a member of the nylon family. This material has not yet been announced, but it is under investigation in the plywood industry where excellent experimental results have been obtained. It is as yet too early to prophesy definitely as to what adhesives will be most important after the war, for not only will new materials be available, but economies of those already introduced will have to be worked out.

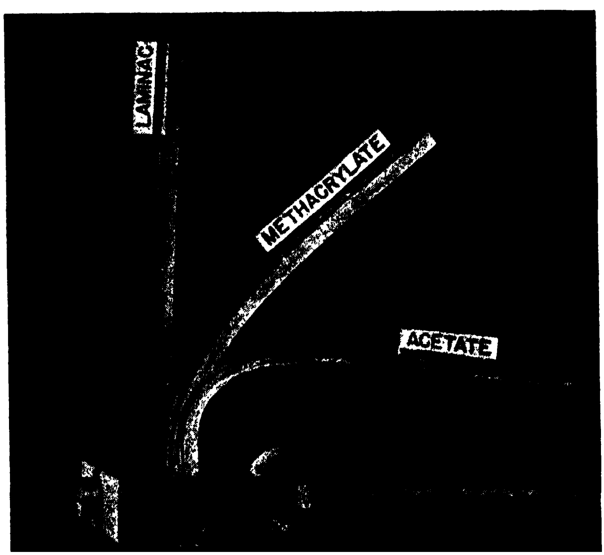
CHAPTER VII

New Laminating Materials

ANHYDROUS THERMOSETTING RESINS

DURING the past few years, new resins have been developed which may be broadly classified as anhydrous thermosetting resins. These meet a long-standing need for laminating at low pressure which permits the use of inexpensive molds and molding equipment to form products having properties in certain respects superior to curved plywood. They also supply a clear cast plastic with superior properties.

Essentially, these new synthetics are casting resins, superior to the thermoplastics in hardness, abrasion and heat resistance.



Courtesy American Cyanamid Co.

FIG. 25. Relative heat resistance of Laminac after 10 min. at 284°F.

However, they have been primarily used for laminating for two reasons:

First — to answer the military demands for large nonmetallic objects of irregular shape, having certain specific properties, particularly electrical for which metals were not suitable, and,

Second — to satisfy the urgent demands of the plastics industry for a contact pressure laminating resin. Parts were frequently needed in such small quantities that production by the conventional high-pressure method was uneconomic.

There are a number of these resins available, and the statements apply generally to the entire group. However, the specific properties which will be mentioned are in a large part those of Laminac, a thermosetting vinyl polyester copolymer, produced by American Cyanamid Company. Taken as a group, these resins are with one or two exceptions quite similar in properties.

Certain of these characteristics make them of definite interest to all fabricators and users of laminated and cast plastics, particularly the aircraft industry.

1. The resin is liquid which may be catalyzed easily and cured rapidly with the aid of heat to form tough solid cast thermoset resins or laminates without pressure.
2. The resin may be cast to form essentially colorless flat and curved shapes which are outstanding in heat resistance and have excellent electrical and physical properties.
3. In laminating, extremely low pressures may be used, which permit the fabricator to use the bag or diaphragm process, simple and inexpensive molds and equipment. In addition, flat laminates can be made by a continuous process.

   The wet process which is used eliminates the conventional drying operation necessary with other laminating resins, such as the phenolics, ureas and melamines, and permits easy arrangement of impregnated fabrics within the mold.
4. In general, laminates of cotton and glass fabrics have excellent physical and electrical properties. These properties, naturally, vary according to type of filler used and resin content, and will be discussed later. However, it should be emphasized

that this type of laminate is outstanding in dimensional stability.

TECHNICAL DATA. These anhydrous thermosetting resins polymerize without the formation of water or other volatile by-products, during the cure. Numerous raw material substitutions are feasible and marked modifications in regard to flexibility, hardness and other properties can be produced by changes in formulation, rather than by additions of plasticizers.

DESCRIPTION OF MONOMER. In the unpolymerized form, these resins vary from the clear and colorless to a light amber and are usually low viscosity liquids.

After the addition of the catalyst, which frequently is peroxide, the product is stable for approximately three to four days; therefore, the catalyst generally is added only to sufficient resin to care for the production requirements of one day.

As the resin changes from a liquid to a solid during the cure, it passes through a soft gel stage. A highly exothermic reaction then starts, which usually makes it difficult to arrest the polymerization at the gel stage and which rapidly brings about a full cure.

These resins are relatively light in weight. For example, the specific gravity of Laminac is 1.1 which is of interest in connection with cost. When originally introduced, the price was relatively high; $0.85 to $1 per lb. With increased usage and larger production, the price had been reduced by early 1944 over 25 per cent. Some resins were then available at $0.65 per lb.

FLAT SHEET LAMINATES. After the addition of the catalyst, which is easily dissolved in the resin by slow agitation, the catalyzed resin is allowed to stand in the covered mixer until all air bubbles have been expelled.

While methods vary widely, generally the base materials, or fillers, are cut to size and shape prior to impregnation, since otherwise it is necessary to cut the wet impregnated material.

With some base materials, it is customary to impregnate each ply separately; other bases of several plies may be impregnated by one application of resin to the assembled laminate. Excess resin is removed and distributed by squeezing. To obtain a properly cured

part it is necessary to cover the impregnated assembly, top and bottom, with cellophane, glassine paper or any other impervious film. This cover sheet extends beyond the sides of the assembled laminate. Any surface air bubbles may be removed by wiping or rolling.

The sandwich thus prepared may then be placed between glass or metal plates, or any other material which will exert sufficient uniform pressure to hold the plies in close contact.

The cure is effected by transferring to an oven heated to approximately 240°F. and takes approximately 20 min.

FILLERS. Various base materials have been used successfully. Glass cloth laminates give such high tensile strength that this fabric has been used extensively. Muslin, canvas, paper and wood have also been used. The fabric bases have been more generally used since some work remains to be done to achieve high strength paper laminates.

PRESSURES. Pressures varying from contact to 100 lb. per sq. in. are used, depending upon the material used as a base, and the resin content desired. Sufficient pressure should be used to ensure the filler is held against all the mold surfaces and to control the resin content in the laminate.

CURE TIME. Laminates of Laminac under 1/16 in. are being cured commercially in less than 15 min. It is relatively simple to establish the proper cure cycle as the reaction is not critical within fairly broad conditions of temperature change.

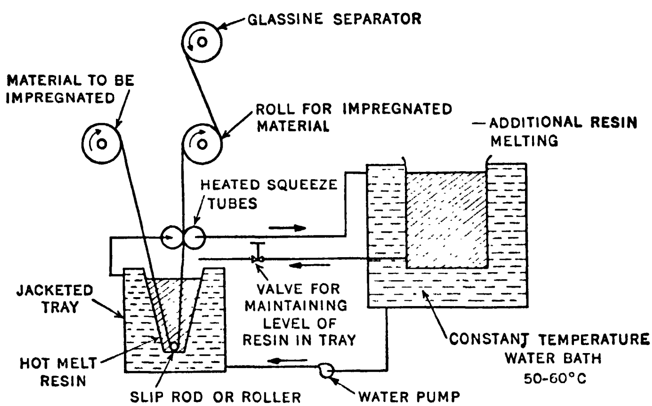
Mold heat transfer is, of course, an important consideration. A much shorter cycle is effected with metal molds than with wooden or plastic molds.

Oven or autoclave efficiency is also a factor, for the proper circulation of air in the oven will provide uniform heating of the molded laminate.

Steam or electrically heated sheet metal male and female dies are used successfully when production quantities warrant the expense.

Some of these resins require longer cures than others, but the range is from 20 min. to 1 hr. in ovens at approximately 240°F. for laminates of 1/16 to 1/2 in. in thickness. Generally, the cure may be shortened by increasing the temperature.

Continuous Process — Flat Sheets. The basic principles of using these resins in laminating flat sheets apply also to work that has been done with continuous production of flat laminated sheets. Figure 26 gives a general outline of a possible procedure.



Courtesy American Cyanamid Co.

Fig. 26. Schematic drawing of hot melt impregnation process. Laminac X4000.

Shaped Laminates. Shaped laminates may be made by two methods:

1. The more common method is to form and fully cure the piece in the desired shape.
2. Simple curvatures may be formed from cured flat laminates by bending while hot.

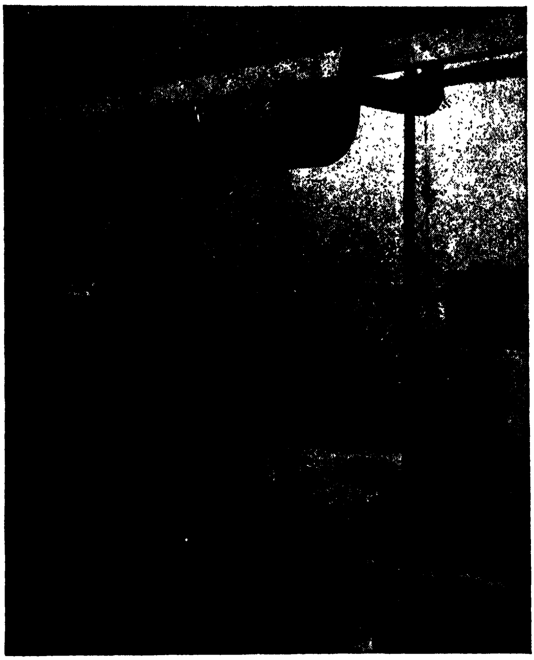
The outstanding advantage of these new resins in the production of large complex shapes with compound curves is twofold: inexpensive molds and inexpensive molding equipment.

Sheet metal, wood, plaster and cement molds may be employed. Low pressures of 5 to 15 lb. per sq. in. ensure that the laminate is uniformly pressed against the mold surfaces and permit control of the percentage of resin in the finished structure.

Some parts are readily fabricated by the use of a sheet metal female mold with a rubber bag inflated to 15 lb. per sq. in., which provides sufficient pressure to produce an excellent structure. In

many cases, tension or stretch pressure on a male mandrel is used when the shape permits.

In one case, the base muslin is passed through a dipping bath of Laminac, excess resin is removed by rolls, and the impregnated cloth is wound around a wooden mandrel. The wrapping tension, plus a shrinkage during cure, provides sufficient pressure to form a very satisfactory laminated tube.



Courtesy American Cyanamid Co.

FIG. 27. Impregnating tank and winding device in use in production of Laminac.

RESINS AS ADHESIVE. One of the most valuable properties, from a fabricator's point of view, is the ability of the Laminac type resin to act as its own adhesive. A complex laminated part may be cured in sections which can then be assembled by using the catalyzed liquid resin as a glue. All that is necessary is to sand the contact points, apply the resin to both surfaces and give the clamped assembly a short cure in the oven. This gives a joint comparable in strength to the laminate itself.

Summary of Laminating. In laminating there are three points of emphasis in the use of these resins:

1. Prompt assembly of the laminate is desirable. For example: a 15-min. assembly time will produce a material of much higher modulus of elasticity and greater rigidity than one laid up in 3 hr.
2. The laminate should be completely covered with an impervious film. This film also serves as a separator to prevent adhesion to wooden molds. Rubber is attacked by these uncured resins and a covering film should be used to protect the rubber, when bag or diaphragm molding methods are used. A film cover strips easily from the cured part, and it imparts a smooth surface to the laminate. The use of this protecting film on compound curved shapes is sometimes difficult. As research continues it is possible that this difficulty may be eliminated. Some fabricators report success with molds sprayed with a suitable coating.
3. With a given base, the physical and electrical properties of a laminate may be varied somewhat, depending upon the percentage of resin used. Naturally, a contact pressure laminate will contain a high ratio of resin to filler, as high as 60 per cent in the case of cotton duck. Some improvement in properties is generally observed when pressures of from 5 to 50 lb. per sq. in. are used.

Physical and Electrical Properties. Electrical properties of the cast resins are excellent. They have low power factors and low dielectric constants at a wide range of frequencies. The dielectric strength is high.

The materials have good hardness values and strength properties, as well as excellent dimensional stability.

Castings. Laminac and other similar resins show considerable promise for the field of casting. Due to their thermosetting qualities, these resins have high heat resistance. For example: The A.S.T.M. heat distortion point of unfilled Laminac is 212°F. These cast resins have considerably higher abrasion resistance than the methacryl-

ates. While they will support combustion, the burning rate is less than that of the methacrylates, in some instances as low as one-third of the methacrylates.

These resins are also highly resistant to chemicals. In solutions at room temperature the 24-hr. pickup of water is only ½ of 1 per cent; gasoline, ¼ of 1 per cent; and acetone, 2½ per cent. While this absorption takes place over long periods, the actual solubility is extremely low. Incidentally, because of this property, laminated auxiliary gasoline tanks are one interesting laminating application.

In cast form, the resins can be machined without difficulty. They are more brittle at room temperature than thermoplastics, but with suitable tools, they may be readily sawed, turned and drilled. Their infusible character facilitates operations in which heat is developed, such as sawing, sanding, grinding and buffing. These operations may be performed at high speeds without a tendency to drag, fuse or gum.

Clarity. Recent developments have brought about water clear materials which are virtually unaffected by ultraviolet light. Plate glass transmits approximately 90 per cent of visible light, whereas these new purified Laminac resins transmit about 87 per cent in the blue band and are comparable to optical glass in the red band.

Heat resistant formulations of Laminac resins can stand 3 hr. at 300°F. with only 2 to 3 per cent decrease in light transmission due to yellowing.

These optical formulations while produced in experimental quantities only should find wide acceptance in the postwar era, since they are only approximately one-half the weight of glass.

Casting Technique. Molds having extremely smooth surfaces are required for casting and the castings should be protected from the air by a cover sheet until gelation has occurred.

The resins have a shrinkage of approximately 10 per cent when cast. Fillers may be used, such as silica flour, diatomaceous earth, glass cloth clippings and canvas clippings. With such fillers, the shrinkage may be reduced materially, and it varies inversely with the volumetric percentage of filler used.

A long cure time, beginning at relatively low temperature, is

necessary to produce satisfactory castings, particularly if the cross section is thick. However, some of the resins may be cast in 3 to 5 hr.; others require from 12 to 24 hours.

CONCLUSION. The anhydrous thermosetting resins, although still in the development stage, have demonstrated certain inherent advantages over medium- and high-pressure resins.

Fabricators who have worked with them feel confident that their potential field of usefulness is very broad. It has been said that they will revolutionize the laminating industry. Whether or not this proves to be the case, they will undoubtedly create a great many new and expanding uses for plastics.

LAMINAC RESIN NO. 4122

PROPERTIES OF UNCURED LIQUID

Specific gravity, at 25°C	1.11
Index of refraction, N_d at 24°C	1.5155
Viscosity, at 25°C, centipoises	165–200
Heat of reaction, during cure, cal/gm	86.3
Stability of liquid, in dark:	
at 25°C	Greater than 6 months
at 40°C	Greater than 30 days
Stability of liquid containing 0.5% Alperox C, in dark:	
at 25°C	Greater than 5 days

LAMINAC RESIN NO. 4122

CLEAR CAST (AEROGLAS)*

PHYSICAL PROPERTIES

Specific gravity, at 25°C	1.23
Index of refraction, N_d at 25°C	1.535
Micro hardness (Bierbaum)	26.3 – 39.1
Rockwell hardness: M Scale	91 – 94
Ultimate tensile strength, psi:	
at −40°C	7270
at 25°C	6270
at 80°C	3850
Modulus of elasticity in tension, 25°C, psi	0.35×10^6
Flexural strength, psi:	
at −40°C	15,300
at 25°C	13,900
at 80°C	6380

* Trade name for clear cast resin.

LAMINAC RESIN NO. 4122 — *Continued*

Modulus of elasticity in flexure, 25°C, psi	0.31×10^6
Compressive strength at 25°C, psi	26,400
Impact strength, Izod notched, per inch notch	0.3 – 0.4
Shrinkage during cure, %	10
Heat distortion point (ASTM)	100°C
Flammability, in./min	0.80

ELECTRICAL PROPERTIES

Power factor, ASTM:	
at 60 cycles	0.011
at 10^6 cycles	0.031
Dielectric strength, ASTM short time test, ⅛ in., v/mil	520
Dielectric constant, ASTM:	
at 60 cycles	4.2
at 10^6 cycles	3.5
Loss factor, ASTM:	
at 60 cycles	0.053
at 10^6 cycles	0.120
Arc resistance, ASTM	90–126

CHEMICAL PROPERTIES

Gain in weight during 24 hr immersion at 25°C, %	
Distilled water	0.46
Aromatic gasoline	0.23
Benzene	0.76
Acetone	2.58

LAMINAC RESIN NO. 4122

LAMINATE

Filler	Fiberglas ECC-11-162
Number of plies	4
% resin	45
Number of plies	4
Catalyst	0.5% Alperox C
Curing temperature	100°C
Pressure used, psi	30
Thickness, in.	0.065
Weight, psi	0.597

PHYSICAL PROPERTIES

Specific gravity, at 25°C	1.70
Tensile strength, psi:	
at −40°C	47,300
at 25°C	41,300
at 80°C	26,070

LAMINAC RESIN NO. 4122 — *Continued*

Elongation immediately before fracture, 25°C, %	3.4
Modulus of elasticity in tension, at 25°C, psi $\times 10^6$	1.34
Rockwell hardness:	
M Scale	84
R Scale	97
Modulus of elasticity in flexure, psi $\times 10^6$	
at −40°C	1.67
at 25°C	1.66
at 80°C	1.35
Compressive strength at 25°C, psi (flatwise)	50,900
Izod impact (edge) ft lb/in. notch:	
Perpendicular	37.9
Parallel	50.0
Dimensional change, mils/in. 2 wk 120°F:	
Perpendicular	0.0
Parallel	0.0
2 wk 85°F 90% RH:	
Perpendicular	−0.7
Parallel	−0.2

Thermal expansion in./in./°C:

	Perpendicular	*Parallel*
80°C	9.5×10^{-6}	12.5×10^{-6}
60	11.0×10^{-6}	8.5×10^{-6}
40	14.5×10^{-6}	8.5×10^{-6}
20	19.0×10^{-6}	13.5×10^{-6}
0	19.5×10^{-6}	12.5×10^{-6}
−20	19.0×10^{-6}	12.0×10^{-6}
−40	18.5×10^{-6}	12.0×10^{-6}

ELECTRICAL PROPERTIES

Power factor, ASTM:	
at 10^6 cycles	0.02
at 25×10^6 cycles	0.04
Dielectric constant:	
at 10^6 cycles	5
at 25×10^6 cycles	6
Dielectric strength, 25°C, v/mil	310
100°C	320
Volume resistivity, ohms	10^{12}

CHEMICAL PROPERTIES

Gain in weight during 24 hr immersion at 25°C, %:	
Distilled water	1.3
Aromatic gasoline	1.0
Benzene	3.0
Acetone	6.9
Gain in weight during 15 min immersion in boiling water, %	0.5

LAMINAC RESIN NO. 4122

LAMINATE

Filler	Cotton duck, 14 oz
Number of plies	25
% resin	38
Catalyst	0.5% Alperox C
Curing temperature	100°C
Pressure used, psi	100
Thickness, in.	0.50

PHYSICAL PROPERTIES

Specific gravity, at 25°C	1.25
Flexural strength at 25°C, psi:	
flatwise	13,400
edgewise	12,900
Deflection at fracture in flexural test, mils:	
flatwise	302
edgewise	279
Compression strength at 25°C, psi:	
flatwise	27,100
lengthwise	17,600
edgewise	16,200
Impact strength, Izod notched, 25°C, per in. of notch:	
flatwise	13.12
edgewise	7.73

THERMOHARDENED RESINS (MR-RESINS)

MR-resins are a new class of thermohardened resinous materials developed by Marco Chemicals, Inc., of Sewaren, N. J., affiliate of Continental Can Company. The MR series includes both allyl and silicone resins.

The MR-resins combine many of the advantageous properties of both the thermosetting and the thermoplastic types of resins. The monomers or intermediate polymers of this class may be converted to their final form by the processes usually applied to the production of the common polymerizable thermoplastic resins. The ultimate polymers so obtained, however, possess the hardness, infusibility and chemical inertness characteristic of thermohardened resins.

Many of the disadvantages of both the thermoplastic and thermohardened resins are avoided by the use of MR-resins. In the monomeric, or intermediate, state of cure, MR-resins are clear polymer-

4 PLY FIBERGLAS ECC-162 LAMINATES

Cure: 30 min in press at 105°C followed by 12 hrs in oven at 150°C

All tests run parallel to warp	Bakelite 16631	Laminac 4122A	Laminac X-4000	Laminac X-4001
Laminate No.	3,683	3,684	3,685	3,686
Resin content, %	42	42	42	43
ASTM flammability, in./min	0.94	0.94	0.85	0.88
Tensile strength, psi				
+80°C	30,600	31,800	32,300	32,400
+25°C	34,000	34,500	35,000	32,800
Rockwell hardness				
M Scale	81	75	90	100
H Scale	90	83	93	97
Bending modulus, psi $\times 10^6$				
−40°C	1.11	1.38	1.49	2.13
+25°C	1.72	1.81	2.18	2.33
+80°C	0.79	0.70	0.75	0.96
Flexural strength, psi				
−40°C	31,600	29,600	28,900	26,800
+25°C	24,400	23,000	27,400	24,200
+80°C	8,100	8,200	13,400	14,800
24 hr absorption, %				
Water	1.7	2.2	1.8	1.6
Gas	1.1	1.3	1.2	0.6
Benzene	2.2	3.5	1.8	1.0
Acetone	5.1	6.1	4.8	3.4
Power factor 10^6 cps	0.021	0.020	0.016	0.014
Dielectric constant 10^6 cps	4.5	4.5	4 2	3.9
Spot arc resistance				
max	132	132	138	132
min	118	96	128	130
av	128	119	132	131

izable liquids ranging from very fluid to highly viscous adhesive compositions that polymerize without application of external pressure at a temperature of 70° to 160°C. (158° to 320°F.) by means of peroxide catalysis. In the finally cured state MR-resins are hard polymers that do not fuse on heating and are not attacked by water or organic solvents. They are hard, abrasion-resistant resins with a high modulus of flexure, and they exhibit a minimum of cold flow. They are dimensionally stable and chemically inert. In their pure

state they may be polymerized to products of high clarity and transparency.

MR-resins may be used for the fabrication of laminated sheets, referred to as Marcolite, and for the fabrication of miscellaneous shaped laminated resin parts including boxes, tanks, or other containers, wing tips, luggage, air ducts, insulating conduits and other articles of special shape. Because of their lightness in weight, high strength, ease of fabrication and general chemical inertness, they offer numerous advantages in such uses over similar articles fabricated from other raw materials. They are well suited to use in place of metals or the high-pressure thermosetting resins that have been used previously in the plastics field.

When used in place of metal, the parts may be fabricated with less man power and without the use of high-cost special forming equipment such as drop hammer forging equipment, hydraulic presses and heavy molds. Soldering, welding and riveting processes are eliminated, and parts of complex contour may be fabricated without pressure by use of low-cost molds of metal, wood, plaster, etc.

Unlike metal parts, Marcolite possesses substantial rigidity and does not dent readily, nor is it subject to rust or chemical corrosion. It is resistant to the corrosive attack of acids, alkalies or other chemicals. Marcolite does not require protective or decorative paint coatings since wide range of colors and decorative designs may be incorporated in the MR-resin laminates simply by coloring the resin or by use of a surface layer of laminating material with a decorative pattern.

When used instead of high-pressure resins, Marcolite may be fabricated without pressure. The high-cost presses capable of exerting, and molds capable of withstanding 1000 to 2000 lb. per sq. in., which are essential for high-pressure resins, are not necessary. Low-cost molds of simple construction, and special hand or machine shaping operations that are not feasible in high-pressure fabrication processes can be used with MR-resins. Sheets of large size and shaped parts of unusual contour or size that cannot be produced from high-pressure resins can be fabricated from MR-resins without difficulty.

Marcolite is much superior in impact strength to molded high-pressure resin products. Moreover, it is equal or superior in strength to most high-pressure laminates and in general is more resistant to water and chemicals. Marcolite has good electrical properties.

The physical and structural properties of Marcolite vary over a considerable range with the type and orientation of the filler material used, and to a lesser extent with the methods of fabrication and the specific type of MR-resin used. In general, the properties of MR-17 type resin laminates are similar to MR-1A type laminates; the MR-17 type being preferred primarily because of its improved fabricating characteristics.

MR-resins have many other uses; for example, they may be cast-polymerized to form clear transparent sheets, rods, tubes or other forms of various shape or contour. These clear polymers are hard, insoluble and infusible, and they are less susceptible to abrasion than the usual types of transparent polymers.

PROPERTIES OF MARCOLITE

	Fiberglas	Cotton	Paper
Moisture absn (%)	0.3	0.5–1.2	3.0–5.0
Gasoline absn (%)	0.0	0.0	0.0
Specific gravity	1.70–1.80	1.40–1.48	1.4
Burning rate (in./min)	0.3	0.44	0.35
Tensile strength (psi)	35,000 45,000	8,500 12,000	13,000
Mod. in tension (psi)	2,000,000 2,300,000	1,000,000	1,000,000
Flexural strength (psi)	38,000	20,000	19,000
Compression strength, flatwise (psi)	58,000	32,000	34,000
Compression strength, edgewise (psi)	22,000	20,000	16,000
Impact notched Izod, ft-lb/in. notch	35	2.9–3.4	0.9–1.0
Impact notched Izod, ft-lb/sq in.	225	18–20	5.5–6.4
Hardness Rockwell M	110	92	93
Shear (psi)	20,000	12,000	11,000
Bearing (psi)	27,000	20,000	20,000
Thermal expansion, 10^{-5}/°C	1.0–2.6		
Heat distn °C	160		
Dimensional stability, (%)	L, W, T = 0, 0, 0		
% Elongation in 2 in. gauge	2.5	3.7–5.0	2.2

These resins also may be used to formulate coating or sizing compositions to be applied to wood, metal, glass, leather, paper or other base materials, and coatings that are inert and possess good weather resistance may be secured. Certain of the MR-resins may be effectively used as adhesives.

The basic properties of various types of Marcolite determined by averaging a series of test data are given on page 180.

RESINS AND GLASS

An important factor required in resins for bonding glass cloth is adhesion of the resin to the glass. Such adhesion has a pronounced influence on the edgewise compressive strength of laminates. The type of resin used also has an important bearing on other properties of glass laminates. The right resin will improve flexural strength, coefficient of expansion, water absorption, hardness and chemical resistance.

For aircraft uses the tensile, compression and shear values of a laminate should be approximately the same. A laminated panel in an airplane in flight is subject to the interaction of a complex series of forces, and the material is liable to fail in its weakest property. A material is needed that has mechanical properties at least as good as those of light metals on a strength-weight basis.

In certain applications, electrical properties are important. To meet such requirements, the resin must have low water absorption and preferably constant electrical properties over a wide frequency range.

Laminates must be prepared for variations in temperatures from $-60°$ to $+170°$F. and for variations in relative humidity from 0 to 100 per cent.

Where the laminates are to be used for exterior parts, such as domes or fairings, a resin with unusually good weatherability must be selected. If the laminates are to be used in air ducts or deicer ducts, a resin with high heat resistance is required. Because few structural materials meet such stringent requirements, it has been necessary to compromise in certain applications for glass cloth laminates. These are equal to the light metals on a strength-weight

basis, but their first applications were on nonstructural parts rather than on primary structural members.

Two principal types of resins have been used for glass laminates for aircraft parts. These may be generally classified as condensation resins and polymerization resins. The condensation resins include the phenolics, ureas and melamines. These are generally applied in solution, and the solvent is evaporated off before molding, thereby leaving a dry impregnated fabric that can be stacked or rolled for storage before laying up. The polymerization resins include the allyls, unsaturated polyesters and styrenes. These are applied in the form of a low-molecular-weight liquid that polymerizes upon heating to a solid form. Consequently, the laminates must be laid up while the resin is still liquid.

Condensation resins are applied by a glue spreader, by dipping or by brushing. The formulated resin should have a minimum pot life of 24 hr. After the fabric has been coated, it is dried at a temperature that will remove the solvent but will not appreciably affect the resin. It may be dried continuously by machine or hung up to dry in batches. The impregnated, dried cloth can then be rolled and stored ready for use. In dried nontacky form, it is easily handled. Templates are placed on the cloth, shapes are cut out, and the pieces are tacked in place on the mandrel with a soldering iron. It should be possible to store the cloth either in rolls or assembled before use for as long as one week.

The polymerization-type resins are ordinarily applied by brushing or dipping. The pieces are laid up wet on the form, where the tackiness helps to hold them in place. This type of operation is more expensive than that with the condensation-type resins.

In order to impregnate the cloth with the proper proportion of resin, the viscosity of the solution must be so adjusted that the correct resin pick-up will result. In the polymerization types, the viscosity also should be sufficiently high so that the resin will not drain while the cloth is being handled and thus result in uneven distribution in the laminate.

Curing is affected by three factors, pressure, temperature and time. In order to utilize the advantages of bag molding, it is necessary to obtain a sound laminate at low pressure. The resins that

have so far been developed will form sound laminates over a pressure ranging from that needed merely to hold the laminate in place to approximately 150 lb. per sq. in. A cure temperature of from 150° to 250°F. is necessary for low-pressure laminating resins because higher temperatures cause deterioration of the rubber used for bag molding. For practical production, the resin must cure at this temperature in a few hours, and a curing time within 1 hr. is desirable. A long curing cycle increases the direct molding cost and involves duplication of forms and equipment to obtain the desired rate of output.

LOW-PRESSURE LAMINATING RESINS. The two classes of resins may be illustrated by data for a phenolic type (condensation resin) and an unsaturated polyester type (polymerization resin). The polyester resin yields a laminate that has somewhat superior mechanical properties; the phenolic resin gives a laminate that is easier to handle in processing and lower in initial resin cost. Table I is a comparison of the properties of these two resins.

TABLE I. PHYSICAL PROPERTIES OF LOW-PRESSURE GLASS-CLOTH LAMINATES:

POLYESTER TYPE RESIN COMPARED WITH PHENOLIC

Property	Typical Low-Pressure Laminating Resin of the Polyester Type	Phenolic
Edgewise compression	44,540–46,670	28,000–32,000
Flexural strength	63,750–71,150	39,000–40,000
Water absorption, 24 hr	0.5%	0.5%
Hardness, Rockwell M	112	85–95
Glass content by weight	55%	45%
Specific gravity	1.77	1.70

The above properties were obtained by laminating at ½ psi for the polyester and 15 psi for phenolic.

Source: Monsanto Chemical Company.

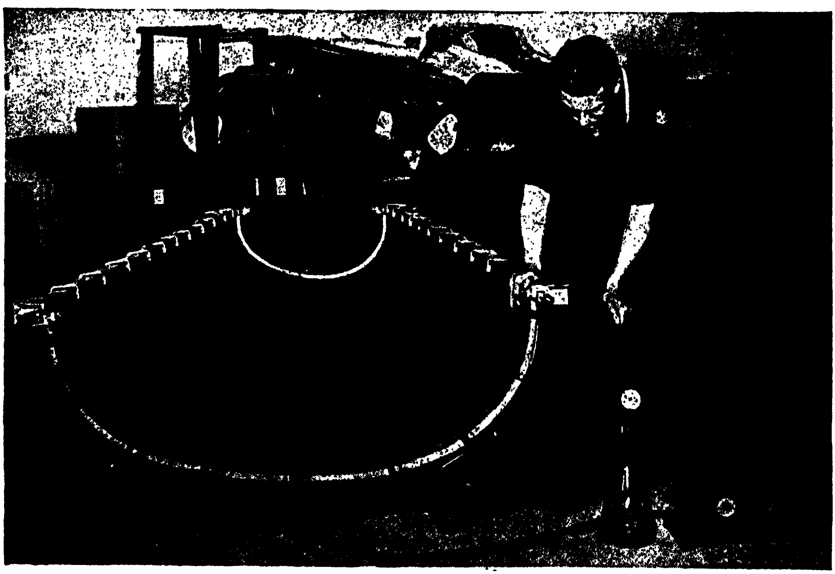
GLASS-REINFORCED PLASTICS

The recent development of plastics reinforced with glass fibers provides a new structural material that differs radically in mechanical properties from most existing materials and opens up a whole

new vista of postwar applications which may in the course of a generation or two alter radically our ways of living.

Many different types of fibers, including cotton, linen, nylon, rayon, silk and glass fibers were being investigated by the Army Air Forces, Materiel Command, Wright Field, in an effort to find a high-strength plastics structural material for use in aircraft construction. Several factors led to the selection of glass fiber as the most satisfactory reinforcing material. The strength-weight ratio of glass fibers is greater than that of other types; they can be produced in continuous filaments, and their properties can be closely controlled, making possible a uniform laminate. Moreover, the impact resistance is high and moisture absorption low. A laminate utilizing fiber glass is therefore light, strong and uniform and has satisfactory weathering characteristics.

In the spring of 1944 successful flight tests were made by an Army basic training plane equipped with glass-reinforced plastics fuselage, side panels and tail cone.



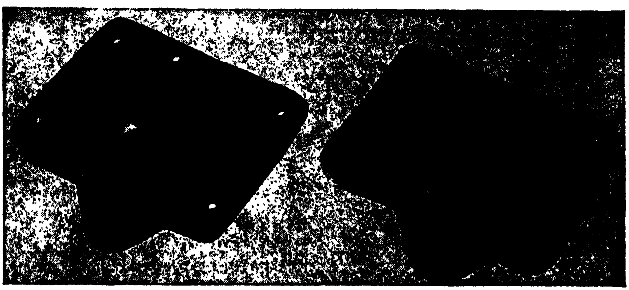
Courtesy Owens-Corning Fiberglas Corp.

FIG. 28. This shows the assembling of a glass cloth fuselage with balsa wood core, plastics bonded.

The fuselage (Fig. 28) was of sandwich construction consisting of balsa wood core between an inner and outer skin of plastics reinforced with fibrous glass cloth. Ground destruction tests of three fuselages of the same design — one of glass-reinforced plastics, one of metal, and one of plywood — indicate that for equivalent weight the glass sandwich fuselage is considerably the strongest.

On a strength-weight basis the glass-reinforced fuselage is 50 per cent stronger than the metal fuselage and 80 per cent stronger than the wooden fuselage now in service. Firing tests indicate that the glass-reinforced fuselage will be satisfactory under gunfire. The material does not flower, and high-explosive projectiles fail to detonate because of its low density.

Plastics, including glass-reinforced forms, have been widely employed in nonstructural applications. The new material, because of its high strength, light weight and ease of molding into intricate



Courtesy Bakelite Corp.

FIG. 29. Low pressure laminates are used for airplane parts. These are aileron hinge fairings.

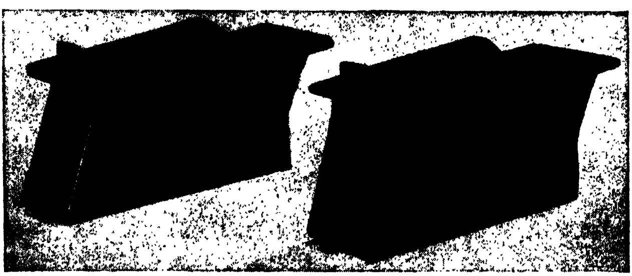
shapes without high pressures, high temperatures or expensive molds, can be used for aircraft parts. This applies also to Formica's glass mat laminates.

The fuselage, side panels and tail cone were fabricated at Wright Field. Research in the fabrication of the glass-reinforced laminates and their physical properties was conducted in the laboratories of Owens-Corning Fiberglas Corporation at Newark, Ohio. Resin manufacturers who cooperated by furnishing resins for the research conducted in the Fiberglas laboratories are: American Cyanamid

Company; Marco Chemicals, Inc.; Plaskon Division, Libbey-Owens-Ford Glass Company; Monsanto Chemical Company; Columbia Chemical Division, Pittsburgh Plate Glass Company; Dow Chemical Company and Bakelite Corporation.

The glass reinforcements employed in fabricating the laminates are heat-treated Fiberglas cloths and short, fine fibers known as Fiberglas flock. The resins were Plaskon 900, Laminac P-4122, MR-1A, Monsanto 38691, CR-39, and CR-149. These resins, in combination with glass fibers, lend themselves to low-cost production methods adaptable to experimental and commercial designs.

Each of the various combinations of glass and resin was fabricated for the test into ¼- and ½-in. thick laminated sheets. The sheets were cured at a pressure of 15 lb. per sq. in. in an electrically heated hot-air oven. Specimens were cut from the cured sheets and were machined and tested. Test results indicate that, on a strength-to-weight ratio, glass cloth laminates possess physical properties comparable with those of a number of the metal alloys now used for aircraft structural parts.



Courtesy Bakelite Corp.

FIG. 30. This shows the comparison between a metal shell ejector (at left) and one made with low pressure laminate.

Tensile strengths were found to be proportional to the amount of glass present in the laminates, and varied from 43,360 to 54,720 lb. per sq. in. Compression strengths as high as 56,820 lb. per sq. in. were obtained. Flexural values ranged between 45,350 and 84,600 lb. per sq. in. Impact strengths of unnotched specimens were from 28.82 to 31.25 ft.-lb. Modulus of elasticity was 2,200,000 lb. per sq. in. Average specific gravity was 1.75. These values are for cross-

PHYSICAL TEST RESULTS — MR-1A FIBERGLAS LAMINATES*

Laminate designation	223	224	309	236	221	241
Filler, Fiberglas No.	OC-63	OC-63	OC-63	ECC-11-127	ECC-11-148	ECC-11-161
Number of laminae	12	12	8	18	10	8
Stack arrangement	Parallel	Crossed 90°	Crossed 90°	Crossed 90°	Parallel	Crossed 90°
Nominal thickness, in.	0.104	0.107	0.107	0.128	0.124°	0.121
Specific gravity	1.96	1.93	1.69	1.81	1.80	1.79
Tension						
Direction of load	With warp				With fill	
Ultimate load, lb	6,390	3,140	2,095	2,840	2,070	2.210
Specimen width, in.	0.604	0.502	0.502	0.502	0.482	0.505
Ultimate load per in. of width per lamina	880	520	520	315	430	550
Tangent proportional limit, psi	50,000	32,000	21,000	26,000	13,000	13,500
01% offset proportional limit	58,000	41,000	25,000	27,500	15,000	15,500
2% offset yield stress		58,000		38,700	30,800	24,300
Ultimate tensile stress	105,000	58,500	39,000	44,200	34,600	36,200
Young's modulus of elasticity, psi	5,960,000	2,800,000	1,900,000	2,100,000	1,500,000	1,900,000
Elongation at failure (% over 2 in. length)	1.8	2.3	2.1	2.6	2.6	2.9
Compression (Edgewise)						
Direction of load	With warp				With fill	
Ultimate load, lb	1,340	1,380	1,580	1,393	1,000	1,200
Specimen width, in.	0.496	0.500	0.495	0.500	0.500	0.500
Ultimate load per in. of width per lamina	225	230	400	155	200	300
Tangent proportional limit, psi	26,100	25,950	21,500	14,000	11,000	10,000
01% offset proportional limit			23,700	15,000	14,000	12,000
Ultimate compressive stress	26,100	26,000	29,000	22,500	16,900	19,600
Young's modulus of elasticity, psi	5,500,000	3,000,000	2,260,000	2,800,000	2,200,000	2,300,000
Deformation (% over 2 in. length)	0.47	0.86	1.38	0.86	0.75	0.93
Manner of failure	Diagonal shear	Diagonal shear	Diagonal shear	Diagonal shear	Diagonal shear	Diagonal shear
Bending (Flatwise)						
Length, width, thickness, in.	5 × 1.02 × 0.102	5 × 0.745 × 0.106	5 × 0.749 × 0.109	5 × 0.751 × 0.128	5 × 0.751 × 0.126	5 × 0.746 × 0.116
Span, in.	3	3	3	3	3	3
Ultimate load at center of span, lbs	138	90	128	105	94	78
Tangent proportional limit, psi	55 000	41,000	45,000	17,000	19,000	19,000
Modulus of rupture, psi	59,300	48,200	64,800	38,400	35,500	34,900
Modulus of elasticity, psi	5,950,000	3,000,000	2,100,000	2,300,000	1,630,000	2,080,000
Bearing						
Hole diameter		0.124	0.124	0.124	0.124	0.124
Nominal bearing strength (4% hole deformation)		28,000	23,500	20,000	29,500	23,300
Ultimate bearing strength, psi		32,100	31,300	38,500	34,800	34,600

* *Iron Age*, July, 1943.

laminated glass cloth. Strength values approximately twice as high may be obtained with parallel-laminated cloth.

Although the problems of the airplane builders have been largely responsible for the search for fundamental data on plastic-Fiberglas combinations, the data accumulated will be of great value to many other industries for peacetime applications.

Dr. Frank W. Preston, Preston Laboratories, Butler, Pennsylvania, recently summarized the significance of new data on combinations of plastics and glass fibers.

In plastics reinforced with glass fibers we have a material having very high strengths, which are apt to go much higher as we learn more about it. This great strength is combined with a very low weight, much below aluminum, so that the strength-to-weight ratio is favorable. Plastic-glass laminates lend themselves to slender forms, to light-weight construction, to rounded contours, sweeping and reversed curves, and to "streamlining" generally.

We are coming to a time when relatively gigantic machines, comparable to those of the steel mills, will fabricate some plastic elements. But that time still lies ahead. We first have to fabricate by less costly means, and learn how to produce large elements — say the whole body of a canoe or row boat, the fuselage or wings of a plane, the body of an automobile, a table or chair, and many other things, with a maximum of strength and a minimum of weight.

We believe that in plastic-glass combination there is in sight a new material of construction, calling for new standards of ingenuity among engineers, and offering to the plastics industry vast possibilities. It will call for new techniques of fabrication, and will achieve many results hitherto impossible. What we have found to date is only a beginning. The strengths and properties so far realized do not by any means represent what is ultimately possible. But the result is already substantial. We have every reason to believe the ultimate results will be phenomenal.

Resins for Low-Pressure Laminating. The plastics laboratory of General Electric Company recently completed an extensive investigation to determine which types of resins are best suited for low-pressure laminating. As a result they have selected phenolic liquid resin A, phenolic solid resin B, and a modified aminoplast resin. Phenolic resin A is a highly condensed, nearly neutral liquid resin which is stable and mechanically strong in the cured state. Phenolic solid resin B is a molding compound resin which was chosen because of its exceptional strength characteristics. It was prepared for treating the filler by dissolving in alcohol to the desired gravity. The modified aminoplast resin is a more recently developed

liquid adhesive which is catalytically accelerated during the curing operation.

These three entirely different types of resins were evaluated. The basic work was done with a standard G-E cotton cloth with good strength and a fair amount of formability. Pressures used included low pressures already available and those potentially available up through the beginning of the high-pressure range (1000 lb. per sq. in.). The bulk of low-pressure laminating is now done at 65 to 75 lb. per sq. in., especially in those systems that use steam as both the heating and the hydraulic medium.

From the investigation it may be concluded that the use of 52 to 55 per cent resin in a pressure range of 100 to 300 lb. per sq. in. would give about the maximum in mechanical and physical properties without resorting to the high-pressure range. Moreover, at the present limits of 65 to 75 lb. per sq. in., the effective utilization of potential strength is quite high, especially in the liquid phenolic resin. The use of the aminoplast resin can be justified only where a lower curing temperature is imperative and the lower strength and lower moisture resistance are acceptable.

A comparison of grade C high-pressure phenolic laminate with various laminates bonded with liquid phenolic resin A at 65 lb. per sq. in. has been made in Table II. The properties exhibited by the cotton-cloth low-pressure laminate are generally slightly lower than those of the grade C laminate, although the difference is minute compared with the difference in pressure. Compared also with grade C, the low-pressure laminate of cotton cloth with liquid phenolic A is practically as strong in tensile and flexural strengths and approximately half as strong in compression and tensile modulus. The comparison in moisture absorption is favorable. With a saturating kraft or 100 per cent rag-paper base, the strengths not only increase but are actually higher than those of the grade C laminate, which is a cloth-base material. The tensile and tensile modulus values for the rag-paper filler are nearly twice as great as those of the grade C.

As is to be expected, the laminated glass cloth gave high values, but they are largely offset by the high resultant gravity of 1.73. The use of cotton fill in the glass cloth aided bonding. However, the glass

TABLE II. COMPARISON OF PHENOLIC LAMINATED FILLERS

Liquid phenolic resin A bonding at 65 psi compared to grade C high-pressure phenolic bonding

Property	Grade C Laminated at 1000 to 1500 psi	Cotton Cloth Laminated at 65 psi	Saturating Kraft Laminated at 65 psi	100% Rag Paper Laminated at 65 psi	Glass Cloth Cotton-fill Laminated at 65 psi
Tensile strength, psi	10,000	8,250	12,600	19,400	33,000
Tensile modulus, psi	500,000–1,000,000	327,000	810,000	900,000	1,560,000
Flexural strength, psi	20,000	18,250	24,500	26,550	42,000
Compressive strength, psi	40,000	27,400	34,500	46,600	59,000
Resin content, %	45–50	54	54	52	43
Specific gravity	1.36	1.30	1.35	1.38	1.73
24 hr H_2O absorption (untreated surfaces)	1.5	3.35	1.3	1.25	1.17

COMPARISON OF HIGH-STRENGTH PLASTICS, WOODS AND METALS

Type of Material	Specific Gravity	Tensile Strength psi	Ratio of Tensile Strength to Sp. Gr. psi	Compressive Strength psi	Ratio of Compressive Strength to Sp. Gr. psi	Modulus of Elasticity in Tension (E_t) psi
Laminated 1	1.35	12,500	9,250	35,000	25,900	1.0×10^6
Laminated 2	1.35	11,000	8,000	35,000	25,400	1.05×10^6
Laminated 3	1.35	11,000	8,150	31,000	23,000	1.05×10^6
Laminated 4	1.35	16,000	11,800	38,000	28,100	1.7×10^6
Stainless Steel (18–8)	7.85	185,000	23,600	150,000(a)	19,100	30×10^6
Chrome Molybdenum Steel (Heat-Treated)	7.85	180,000	22,900	150,000(a)	19,100	29×10^6
Aluminum Alloy (24ST)	2.80	62,000	22,100	40,000(a)	14,300	10.4×10^6
			25,400	35,000(b)	19,300	6.5×10^6
Magnesium Alloy (AM-585)	1.81	46,000				
Aircraft Spruce (Douglas Fir)	0.43	10,000	23,300	5,000	11,600	1.3×10^6
Birch Plywood	0.80	13,100	16,400	5,700	7,100	1.4×10^6

(a) Yield point in compression (b) Yield point in tension

SPECIFICATIONS OF HIGH-STRENGTH PLASTICS

Designation on Charts	Specifications			Type and Characteristics	Principal Uses
	Army	Navy	NEMA		
Laminated 1	HH-P256 or 71–484 Type II Grade LE	17-P-5 Type FBG	Grade LE	Fine weave fabric base. High moisture resistance, tough, good machinability, good dielectric strength.	Structural and mechanical parts where higher strength than paper-base is required.
Laminated 2	HH-P256 or 71–484, Type II Grade C	17-P-5 Type FBM	Grade C	Heavy-weave canvas base. High strength, high impact, tough, easy to machine.	General purpose for mechanical parts. Widely used in gears. Not recommended for electrical uses.
Laminated 3	HH-P256 or 71–484 Type I, Grade XX	17-P-5 Type PBG	Grade XX	Cotton fiber paper base. Good electrical and mechanical properties. Can be drilled, tapped and machined.	Structural and mechanical parts in fairly humid conditions. Avoid excessive splitting stresses.
Laminated 4	HH-P256 or 71–484, Type I, Grade X	17-P-5 Type PBM	Grade X	Kraft paper base. High strength, good electrical properties, low cost. Machinable.	Structural and mechanical parts not subject to high humidity or excessive impact. Simple machined and other mechanical parts with medium stresses.

SPECIFICATIONS OF HIGH-STRENGTH PLASTICS — (*Continued*)

Designation on Charts	Specifications			Type and Characteristics	Principal Uses
	Army	Navy	NEMA		
Molded 1		Type CFI		Chopped fabric base. High impact strength, good mechanical properties.	High-strength general purpose molded parts.
Molded 2				Chopped (coarse to medium) fabric base. Good mechanical properties.	General purpose; recommended for pulleys, etc. Not recommended for severe electrical applications.
Molded 3				Chopped fine fabric; readily moldable; high moisture resistance.	Suitable for intricate molded designs; chemical resistance. Not good under severe impact.
Molded 4				Chopped heavy fabric base.	General purpose molding compound for electrical and mechanical uses. Not recommended for severe electrical applications, nor for intricate designs.

is so difficult to treat and handle that its use is not advisable except in limited applications.

All in all, the low-pressure laminates compare favorably with high-pressure laminates mechanically and can be used in complex shapes. Perhaps the greatest advantage of low-pressure laminating is the much more efficient utilization of laminate fibers because of the lower distortion and rupturing.

Meanwhile the search for better resins and fillers goes on hand in hand with improvements in manufacturing techniques. The laminator has been forced to find a satisfactory material first, then develop a superior one later. Properties that low-pressure laminates will probably be called upon to exhibit in the near future are stability under wide temperature range, adequate bearing strength, tensile strengths of 30,000 lb. per sq. in., modulus of elasticity as near 3,000,000 lb. per sq. in. as possible, and adequate vibration and moisture resistance. From improvements already made, the extensive use of low-pressure laminates as structural members seems not too remote a possibility.

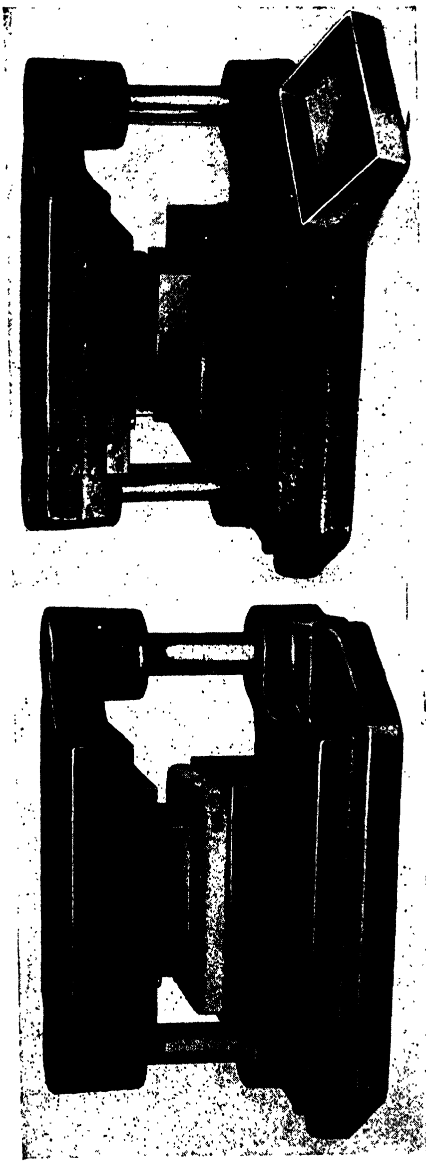
FORMING THERMOSETTING LAMINATES

During the last few years a new method of forming thermosetting laminates which permits flat laminated sheets to be shaped after curing has been developed. This method has found many applications in the aircraft industry and may find postwar uses in the automobile, radio and furniture industries.

Forming is accomplished by subjecting the sheet material to a high temperature over a short period, then forming quickly in a mold. The process is described as follows by The Formica Insulation Company:

Different types of heating media may be used, radiant heat with infrared bulbs, circulating hot air, contact with a hot plate and immersion in a heating liquid or molten alloy, to mention a few.

The blank to be formed must be heated until it is in a pliable condition. Definite temperatures and time must be determined for each job as they vary with the thickness of the material and the type of finished product. Once a satisfactory forming temperature has been determined, it should not be allowed to vary more than a few



Courtesy Columbian Rope Co.

FIGS. 31 and 32. These two views illustrate one method of molding prepared, uncured bats. At the left, the bat (in this case a pre-cut bat of Co-Ro-Lite) is in place in press. At the right, the press has descended and formed the tray as shown.

degrees in either direction. To convert the forming stock from its rigid state to a formable condition, it is exposed to the heat until it is limp and pliable, but not long enough to cause blisters to form. When using a hot air oven heated to 450°F. a 1/16 in. blank of forming stock will be ready to form in 45 sec. heating time and may blister if left in the oven as long as 60 sec. A blank of 3/8 in. material will require approximately 5 min. in the oven. Overheating of the material will cause blistering while underheating will reduce the formability.

When the material becomes pliable it may be removed from the heat and formed to the desired shape by means of molds or bending forms. Molds or forms may be constructed of hard wood, metal or plastic materials, depending upon the complexity of the finished product. Metal is to be recommended when great numbers of the parts are to be made. The pressure required to form this material will depend upon the size, the type of operation and the thickness of the sheet. This will vary from a few pounds for simple bending to several hundred pounds when drawing thick sheets. This pressure can be exerted in various ways, of which hand arbor presses, air arbor presses and hydraulic presses or cylinders have been successfully used.

The total time interval from removal from heating medium to complete closing of the form or mold should be as short as possible and should never exceed 15 sec. The material must be allowed to cool in the form or mold until it will retain its shape upon removing. This period may be shortened by forced cooling with air or water.

CHAPTER VIII

New Applications of Wood and Paper

WOOD AND PAPER-BASE PLASTICS[1]

WOOD and wood products are becoming increasingly important as plastics raw materials. Until recently they were used almost exclusively in the form of wood flour and wood pulp fillers for molding compounds and pulp preforms and in the form of paper for paper-base, nonstructural laminates. Wood is now finding use as the continuous phase in resin-treated uncompressed wood (Impreg) and resin-treated, compressed wood (Compreg). The plastic properties of the lignin constituent of wood are beginning to be utilized. Wood is being partly hydrolyzed to free the lignin and remove undesirable hemicelluloses so that it lends itself better to the making of molding powders that contain but a small per cent of phenolic resin. The resin economy of wood is due to the fact that the lignin serves as a plastics constituent (hydroxylin). Improved resin-impregnated paper-base laminates are being made that have practically twice the strength of earlier commercial paper-base laminates (Papreg).

All these newly developed materials have strength properties comparable to or well above those of former plastics, and some of them are sufficiently strong for various military and peacetime structural uses.

The description of these new plastics presented here is limited to the phase of the developments being carried on at the Forest Products Laboratory. This presentation is necessarily further limited to generalities, because the detailed description of the processes for making most of these products is now classed as restricted government information that can be disclosed only to citizens who require

[1] Prepared in cooperation with Dr. Alfred J. Stamm, Principal Chemist, Forest Products Laboratory, Forest Service of U. S. Department of Agriculture.

the information for war production and who have pledged protection.

IMPREG

A number of desirable properties can be imparted to wood by the forming of synthetic resins throughout the structure from resin-forming constituents of low molecular weight that have an affinity for wood. Although the hardness and compressive strength properties of wood can be improved by mechanically depositing any solid material within the structure, permanent dimensional stability and related properties have been successfully imparted to the wood only with a few specific resinoids under specific treating conditions. This is because materials such as fats, waxes, natural resins and appreciably preformed synthetic resins, because of their large molecular size and their lack of polarity, show no tendency under normal treating conditions to penetrate the cell-wall structure of wood and no tendency to bond to the wood. Forest Products Laboratory tests have shown that any water resistance these materials give to wood is entirely mechanical in nature. They cut down the rate at which water can traverse the structure, but they do not change the final amount taken up and, consequently, do not reduce the equilibrium swelling. Their failure to accomplish this is primarily due to their lack of affinity for wood. One slight flaw in an internal coating will allow water to work its way between the fibrous structure and the coating and disperse itself throughout the continuous structure. It thus becomes apparent that a treating material with an affinity for the wood greater than that of wood for water should be used. Unfortunately, all such materials in themselves have a high affinity for water. This difficulty has been solved with treating agents that are selectively absorbed within the intimate cell-wall structure of wood and can subsequently be converted to water-insoluble resins within the wood structure while remaining permanently bonded to the structure.

The most effective treating agent thus far found is a phenol-formaldehyde, water-soluble resinoid that is not advanced beyond the phenol-alcohol stage. Resorcinol can be substituted for the phenol or furfural for the formaldehyde without loss of effectiveness. All

urea-formaldehyde resinoids tried have proved to be too highly prepolymerized to penetrate the structure adequately, with the exception of dimethylol urea. Even this material when polymerized within the structure reduced the swelling and shrinking on an equilibrium basis to only 60 per cent of normal in contrast to reductions to 30 per cent of normal effected by phenol-formaldehyde resin. None of the thermoplastic resins or thermoplastic resin-forming systems thus far tried has effectively reduced the swelling and shrinking of wood, presumably because none of them has the desired affinity for the wood.

The chemical affinity of wood for a resin-forming system can be gauged by the degree to which the resin-forming solution swells wood beyond the swelling caused by water alone. A 40 per cent aqueous solution of phenol-formaldehyde resinoid will swell wood about 20 per cent more than does water. When the highly swollen wood is dried and the resin is formed within the structure by the application of heat, considerably less than normal shrinkage occurs. The oven-dry treated wood has a volume about equal to that of the green untreated wood. When an amount of resin equivalent to 30 per cent of the dry weight of the untreated wood, an amount that causes practically the optimum reduction of swelling and shrinking, is formed in the structure, the specific gravity of the wood is increased only 18 per cent rather than 30 per cent.

Difficulty has been encountered in properly distributing resin-forming chemicals throughout the structure of massive pieces of wood. The treatment appears practical only for veneer. The value of antishrink treatments of veneer that is normally built up into plywood is questionable because in cross-banded plywood, the fiber direction of one ply restrains the across-the-fiber dimensional changes of the adjacent ply, thus mechanically reducing such changes. Swelling and shrinking cannot, however, be prevented mechanically. The mechanical restraint merely changes the direction of swelling and shrinking. If the wood is prevented from swelling normally in the sheet directions, it will swell in the thickness direction or internally into the fiber cavities. When normal plywood takes up and then loses moisture, the plies are continually working and, as a result of the unevenly developed stresses, face checking is more

serious than in solid boards. Resin treatment, which reduces the swelling and shrinking to about 30 per cent of normal, reduces the stresses to such an extent that checking is practically eliminated. A striking contrast was apparent between resin-treated and untreated surfaces of two panels of Douglas-fir plywood that were exposed to the weather for six months without any surface finish. The face checking of fancy crotch veneer for use in furniture and paneling can be similarly reduced by treatment with a phenolic resin.

The treatment of wood with stabilizing resins also imparts appreciable decay and termite resistance. A specimen of three-ply Douglas-fir plywood with treated faces and an untreated core was immersed for six months to a depth of half its length in a field where decay and termite action on wood are severe. There was little sign of decay, but a great deal of termite action. The termites in a frontal attack found the resin-treated faces not to their liking and so tried a flank attack. They practically cleaned out the untreated core. Similar specimens that were edge-coated with resin and those in which all the plies were treated were still sound after a two-year exposure. Decay and termite action are reduced because the treated wood will not take up enough water within the cell-wall structure to support decay rather than because of the toxicity of the resin.

The treatment of wood with stabilizing resins increases its electrical resistance as a result of the reduced hygroscopicity. Dry wood is an excellent electrical insulator, but it loses its resistance properties rapidly with an increase in moisture content. At 30 per cent relative humidity the electrical resistance of the treated wood is about 10 times that of untreated wood, and at 90 per cent relative humidity it is about 1000 times as resistant.

Resin treatment also increases the acid resistance of wood, but it does not improve the alkali resistance.

The treatment of wood with 20 per cent of its weight of resin may increase the compressive strength and hardness by as much as 50 per cent. Most of the other strength properties are affected only slightly.

Impact strength is the only property that is adversely affected. As the resin content of wood is increased, it becomes brittle. More uniform distribution of the resin also increases brittleness. Unfortu-

nately, the best treatment from the standpoint of stabilization is the poorest from the standpoint of brittleness. Normal birch has an Izod impact value of 9 to 10 ft.-lb. per in. of notch, but after treatment with a stabilizing resin this value drops to only 2 to 3 ft.-lb. per in.

Impreg has the following advantages over normal wood: (1) reduced swelling; (2) reduced checking and surface degrade; (3) improved resistance to decay and termites; (4) improved electrical resistance; (5) improved acid resistance; and (6) improved compressive strength and hardness. These improvements are secured at the expense of decreased toughness.

COMPREG

Compreg is resin-treated wood that is compressed while the resin is formed within its structure. Although a number of different resins have been tried in making this material, none has proved as successful as phenol-formaldehyde. There are two types of Compreg: (1) the older form, developed in Europe, which is treated with a spirit-soluble phenolic resin prepolymerized to the stage at which it does not tend to penetrate the cell-wall structure and bond to the polar groups of the wood and, as a result, does not stabilize wood appreciably; (2) the form developed by the Forest Products Laboratory, which is treated with a water-soluble, phenol-formaldehyde resinoid, as in the case of Impreg, to form the resin throughout the cell-wall structure of the wood and bond it to the active polar groups of the wood. The second form of Compreg is much more stable than the first but tends to be more brittle; like Impreg, it has good decay and termite resistance and good electrical resistance.

Forest Products Laboratory Compreg can be compressed to virtually the ultimate compression (specific gravity of 1.3 to 1.4) under a pressure of 1000 lb. per sq. in., using practically any species of wood. The unstable form of Compreg, on the other hand, requires pressures of 2500 to 3000 lb. per sq. in. for the same degree of compression. There is still greater difference in the pressures required to compress the wood of the stable and unstable forms to intermediate degrees of compression. Practically all the softwoods (coniferous woods) and the softer hardwoods such as cottonwood, basswood

and aspen, when treated with a stabilizing resin, can be compressed to about one half their original thickness under pressures as low as 250 lb. per sq. in. This makes possible the compression of Compreg faces and their simultaneous assembly with an untreated or treated and precured core with but slight compression of the core. This type of material, which shows great promise for postwar uses, cannot be made in one operation when the plies are treated with an appreciably polymerized resin, for there is little differential compressibility between such treated plies and the untreated plies.

A high degree of polish can be imparted to any cut surface of the Forest Products Laboratory form of Compreg by merely sanding and buffing the surface. The potential finish exists throughout the structure. All that is necessary to bring it out is to smooth the surface. This easy way of restoring the finish would be an advantageous property of Compreg or Compreg-faced furniture. The natural finish is highly resistant to such organic solvents as alcohol and acetone, which destroy most applied finishes.

The water absorption of Forest Products Laboratory Compreg is both small and slow. The water absorbed by a 3 in. × 1 in. × ⅜ in. specimen (1 in. in the fiber direction) after immersion for 24 hr. is less than 1 per cent. The unstabilized or less stabilized forms may absorb 6 per cent or more of water under the same conditions.

Forest Products Laboratory Compreg will swell only 4 to 7 per cent in thickness upon prolonged immersion in water at room temperature. Blocks less than 1 in. long in the fiber direction will hardly come to swelling equilibrium when soaked in water at room temperature for a year. When dried to the original moisture content Compreg will practically regain its original dimensions, indicating that the loss of compression is negligible.

The unstable form of Compreg not only will swell about three times as much in thickness as the stable form, but will swell much more rapidly and also lose a large part of its compression. The more rapid swelling is presumably due to the fact that water is sucked into the structure as it recovers from compression and as a result is distributed throughout the structure much more rapidly than by diffusion alone. The combined swelling and recovery from compression of the older form of Compreg 1 in. long in the fiber direction may

be as much as 20 per cent in several weeks. One half to two thirds of this dimensional change may be due to recovery from compression.

Most of the mechanical properties of the two forms of Compreg are similar and, in general, vary in about direct proportion to the compression. When wood is compressed to one third of its original volume, its tensile strength, modulus of rupture in bending, and modulus of elasticity are about trebled, irrespective of whether the wood contains resin. Resin treatment prior to compression improves only the compressive properties and the shear strength in a plane at right angles to the direction of compression. Probably neither of these improvements is sufficient to warrant resin treatment unless it is accompanied by other improvements such as that of dimensional stability. Table I gives the normal strength properties of Compreg in round figures.

The impact strength of Compreg, like that of Impreg, decreases with an increase in the resin content and the intimacy of distribution of the resin, although impact strength, unlike other properties, will vary somewhat with variations in the processing conditions. Overheating during drying after resin treatment or in the pressing process tends to make the product more brittle. Under carefully controlled conditions, the stable form of Compreg can be made (from birch) with an Izod impact value of 5 to 7 ft.-lb. per in. of notch. The unstable Compreg, on the other hand, will have an Izod value of 6 to 9 ft.-lb. per in. of notch.

Compreg can be made from a great variety of woods, including such normally inferior species as cottonwood, and still have properties that approach the optimum values. The only species to be avoided are the naturally resinous woods, such as oak or southern pine, and those that are extremely difficult to treat.

Compreg can be machined easily with metalworking tools but not with woodworking tools. It is therefore desirable to rough out the shape of objects prior to compression, using woodworking tools, and then compress them to final shape in some form of mold. A technique has been developed at the Forest Products Laboratory. Treated, uncompressed plies are glued up into a blank of the correct size with a phenolic glue under conditions such that the treating resin is not cured and the bonding resin is only slightly cured. The

shearing strength of such a block is not great, but the block is sufficiently strong so that it can be carved or turned under favorable conditions. A Michigan company is using with success a method to mold propellers from these blocks for the ground-testing of airplane motors and airplane serial masts. An airplane tail wheel has been successfully molded in this way to pass all static test requirements. The technique could be readily applied in the molding of pulley and gear wheels by stamping out the correct sections in the plane of the wheels from the individual plies and rotating these with respect to each other in the assembly as desired. Although wood is not moldable in the sense that a molding powder is, it is surprisingly subject to molding under proper conditions.

A recently developed process of which nothing at present can be divulged makes possible the production of a highly stable form of compressed wood without the use of any impregnating resin.

HYDROXYLIN

Lignin is the plastic in nature that cements the cellulose fibers of wood together. A mild hydrolysis treatment breaks the cellulose-lignin bond of wood, freeing the lignin so that it can be used to rebond the cellulose fibers. Wood waste, preferably hardwood sawdust or mill waste, can be hydrolyzed by several different methods. The procedure that has received the greatest attention at the Forest Products Laboratory is a hydrolysis with dilute sulfuric acid in a rotary digester at a steam pressure of 135 to 200 lb. per sq. in. for 10 to 30 min. Besides breaking the cellulose-lignin bond, the hydrolysis treatment converts the hemicelluloses to sugars. These sugars, together with the acid, are washed out of the hydrolyzed wood and may be fermented to grain alcohol, thus giving a valuable by-product. The residue constitutes 50 to 60 per cent of the weight of the original wood. As a result of the removal of part of the cellulose, the lignin content is increased to 35 to 40 per cent.

After drying, the hydrolyzed wood is quite brash and can be readily ground to a powder, preferably of 40 to 100 mesh. Although the lignin in hydrolyzed wood can be made to flow sufficiently for the molding of some simple objects by merely adding small amounts of water and pressing at 375°F., the flow is not adequate to give a

product that is sufficiently coherent to stand long water immersion. Similar results are obtained when nonresinous plasticizers for lignin are used in place of water, even though they reduce the molding temperature. It is therefore necessary to use auxiliary plastics or plastic-forming constituents, together with a plasticizer for lignin, when the added plastic material does not also serve as such. The most suitable material found in the earlier work that served both functions is a mixture of 8 per cent aniline and 8 per cent furfural with approximately 84 per cent of hydrolyzed wood and a small amount of mold lubricant such as zinc stearate. Molded products with good mold definition, water resistance, acid resistance and electrical and mechanical properties can be obtained by pressing at 300°F. for 3 min. (in the case of small objects) at 3000 to 4000 lb. per sq. in. Because the product is semithermoplastic, it must be cooled somewhat in the mold.

The flow of this molding powder is not so great as that of the general-purpose commercial molding powders. This, together with the fact that the product cannot be drawn hot from the press, led to further research on the plasticizing of hydrolyzed wood. The best flow properties so far obtained have been with a molding powder containing 25 per cent phenolic resin and 75 per cent hydrolyzed wood. With this combination, the flow properties and the properties of the product are comparable with those of general-purpose molding compounds, containing 50 per cent phenolic resin and 50 per cent wood flour. The fact that only half as much phenolic resin is required with the hydrolyzed wood as with the wood flour indicates that the lignin of the hydrolyzed wood imparts plastics properties to the product.

The hydrolyzed-wood phenolic-resin molding powders give molded products with flexural strengths ranging from 8000 to 13,000 lb. per sq. in., water absorptions of only 0.2 to 0.3 per cent after 48 hr. immersion in water, and extremely high acid resistance. It appears to be possible to mold this material into thicker flawless sections than can be made of general-purpose commercial molding powders. The material is now being tested in the molding of sizable objects of industrial importance.

If chips rather than sawdust are used as the raw material and the

hydrolyzed product is abraded to a fiber rather than ground to a powder, it can be formed into a sheet on the paper machine. These sheets, with only a small amount of phenolic resin, can be compressed together into thick panels. The panels have considerably higher flexural strengths than panels made from the molding powder because of the reinforcing action of the much longer cellulose fiber.

PAPREG

Paper laminates treated with phenolic resins have been used for years, chiefly for electrical insulating panels and for other nonstructural uses that do not require exceptional mechanical properties. The manufacturers, in developing these materials, have approached them primarily from the resin standpoint. Forest Products Laboratory is now developing paper-base laminates in an attempt to find the most suitable paper for any purpose. Within six months after the research was started, a paper-base laminate was developed that possessed several properties double those of the former laminates.

Data on types of paper and modifications in processing are as yet insufficient; however, suitable papers are now being produced by several different paper mills.

The term "parallel laminated" indicates that in all the sheets making up the panel the machine direction of the paper runs the same way. Paper made on a paper machine is always stronger in the machine direction than across the machine direction. The difference may be as much as twofold. When isotropic properties are sought in the laminate, alternate sheets are crossed as in plywood. Cross-banded Papreg differs from plywood and Impreg and Compreg with plywood construction in that the strength properties are not so seriously reduced below the values for parallel-laminated material. Because veneer is from twenty to forty times as strong in tension in the fiber direction as across the fiber direction, the tensile strength of plywood depends almost entirely on the longitudinal plies. Cross-banded Papreg has strength properties ranging from two thirds to three fourths of those for the parallel-laminated material, in contrast to the strength properties of cross-banded Compreg, which are only about one half as high as its parallel-laminated

values. Many strength properties of parallel-laminated Compreg and Papreg are much the same. Cross-banded Papreg is superior in almost all strength properties to cross-banded Compreg.

Papreg has strength properties adequate for a large number of semistructural uses and some structural uses. As a structural material, its brittleness seems to be its most serious handicap. Compared with ordinary plastics, it has quite good Izod values, but it is definitely inferior in this respect to fabric and glass fabric laminates. It is, however, superior to fabric laminates in practically all other strength properties.

Because of its low elongation, Papreg is not so easily molded to double curvatures as are fabric laminates. It has been successfully used, however, in molding of quite intricate objects with only a limited amount of goring and tailoring.

Work is now under way on incorporating other resins, both

TABLE I. NORMAL APPROXIMATE STRENGTH PROPERTIES OF PARALLEL-LAMINATED BIRCH COMPREG WITH A SPECIFIC GRAVITY OF 1.35*

Property	Value
Tension:	Psi
Stress at proportional limit	22,000
Maximum strength	32,000
Modulus of elasticity	3,500,000
Flexure:	
Stress at proportional limit	21,000
Modulus of rupture	36,000
Modulus of elasticity	3,500,000
Compression parallel to grain:	
Stress at proportional limit	16,000
Maximum strength	24,000
Modulus of elasticity	3,500,000
Johnson double shear, parallel to grain and perpendicular to laminations	7,000
	Ft-lb per in.
Izod impact: †	
Face-notched	3 to 9
Edge-notched	2 to 7

* The properties given, with the exception of impact strength, are about the same for both stabilized and unstabilized Compreg and do not vary appreciably between species.

† Three to 7 ft-lb per in. of notch for stabilized Compreg (face notched). Six to 9 ft-lb per in. of notch for unstabilized Compreg (face-notched).

natural and synthetic, in paper-base plastics primarily to make the product cheaper and also with the objective of building up the toughness without too great sacrifice in water resistance and other mechanical properties. Details on this phase of the work are not yet available.

CONCLUSIONS. It is obvious from this array of products that wood is making an important place for itself in the plastics field. Although wood and its constituents serve mostly as the structural or filler part of these plastics, wood and wood products show promise of invading the resin field. Lignin and Vinsol (a rosin-purification residue) are promising resin diluents. It is also of interest that phenols, furfural, and other resin-forming constituents are obtainable from wood by destructive distillation and hydrogenation processes. It does not require great imagination to visualize a self-contained industry that would use wood almost exclusively in the manufacture of plastics. Timber would enter at one end of a plant and molding powder or even complete moldings would issue from the other.

TABLE II. APPROXIMATE PROPERTIES OF PARALLEL-LAMINATED PAPREG

Property	Value
Specific gravity	1.38
	psi
Tension:	
Maximum strength	36,000
Modulus of elasticity	3,000,000
Flexure:	
Modulus of rupture	30,000
Modulus of elasticity	3,000,000
Compression:	
Parallel to grain	17,000
Flatwise perpendicular to grain	40,000
Edgewise perpendicular to grain	15,000
Johnson double shear, parallel to grain, perpendicular to laminations	13,000
Bearing strength	27,000
	Ft-lb per in.
Izod impact:	
Face-notched	5.0
Edge-notched	0.8
Hardness (Rockwell)	M 100
Water absorption (24 hr)	6 per cent

TABLE III. MECHANICAL PROPERTIES OF A BOARD MADE WITH HIGH-DENSITY KRAFT PAPER

This paper is impregnated with 21% aqueous phenol-formaldehyde resin and pressed at 2000 psi.

Density, gm per cu cm	1.47
Tensile strength, tons per sq in.:	
Machine direction	16.5
Cross-wire direction	10.7
Mean	13.6
Shear strength, tons per sq in.:	
Perpendicular to laminations	7.5
Parallel to laminations	2.0
Parallel to edge of sheet	7.8
Compressive strength, tons per sq in.	11.5
Young's modulus (psi)	
Mean of two directions	2.1×10^6

PLYWOOD

Although not strictly a new material, plywood has recently undergone extensive improvements that adapt it to an ever-widening field. Waterproof phenol-formaldehyde adhesives, introduced in 1935, are the basis for recent important developments in plywood.

Several new types of plywood adhesives, among them the melamines and resorcinol, should become commercially available in the near future, although they may not be able to compete for some time on a cost basis with the ureas and the phenolics. A member of the nylon family is reported to be one of the most promising new adhesives.

Figures based on Douglas-fir plywood (which accounts for about 70 per cent of total plywood output), indicate that production of plywood since 1924 has just about doubled every five years. This high rate of growth has been accelerated in recent years as exterior uses of plywood increased the total market. The exterior type developed in 1935 was not produced on a large scale until 1939. Aided by war demand, fir plywood production increased from 1,000,000,000 sq. ft. in 1939 to nearly 2,000,000,000 sq. ft. in 1942.

Plywood will undoubtedly find new outlets after the war, particularly in housing, furniture, small boats and airplanes.

TABLE IV. TOTAL PLYWOOD PRODUCTION

	1939		1937		1935	
	Total* Value	Quantity Reported M sq ft	Total* Value	Quantity Reported M sq ft	Total* Value	Quantity Reported M sq ft
For utility purposes.....	$40,163,768†	1,148,884	$30,017,643	928,430	$17,860,124	460,656
For decorative purposes.	13,709,868	98,124	15,494,477	118,600	9,233,738	121,998
	$53,873,636	1,247,008	$45,512,120	1,047,030	$27,093,962	582,654

Source: U. S. Department of Commerce.

* Includes some value for which no quantity figures are given.

† Includes $29,650,925 Douglas-fir plywood, value of 955,495 M sq ft.

Douglas-fir plywood is principally used for general utility purposes, including construction, boxes and prefabrication; many hardwoods mainly for decorative purposes, including furniture and paneling; southern pine and some other species for both.

"Douglas-fir plywood is a built-up board of laminated veneers in which the grain of each piece is at right angles to the one adjacent to it." (Commercial Standards.) Veneer is thin wood less than $\frac{5}{16}$ of an inch thick.

TABLE V. PRODUCTION OF DOUGLAS-FIR PLYWOOD

(sq ft, on basis of $\frac{3}{8}$-in. rough, 3 ply)

1942	1,800,000,000	1936	700,000,000	1930	305,000,000
1941	1,600,000,000	1935	480,000,000	1929	358,000,000
1940	1,200,000,000	1934	384,000,000	1928	276,000,000
1939	1,000,000,000	1933	390,000,000	1927	206,000,000
1938	650,000,000	1932	200,000,000	1926	173,000,000
1937	725,000,000	1931	235,000,000	1925	153,000,000

Source: Douglas Fir Plywood Association.

PAPER-SURFACED PLYWOOD

An application of paper laminates which, although not new, is becoming important is the surfacing of resin-bonded plywood with paper impregnated with melamine or phenolic resins. This is for the twofold purpose of strengthening and beautifying plywood. Most of the plywood mills and several large paper companies are already experimenting on the procedure. The paper companies or laminators will probably supply treated paper to the plywood producer, and the plywood will be bonded and surfaced in one operation. It is, of course, perfectly feasible to press the papers on finished plywood.

Both kraft and alpha papers may be used, and the thickness of the paper sheet may vary from 3 to 15 mils or more, depending upon the properties desired. Any color combination can be obtained, and the wood grain can be completely or partly concealed by pigmented or kraft papers. By using a melamine alpha paper overlay, the wood grain is brought out through the translucent sheet, giving an extremely attractive appearance.

Large potential markets are interior and exterior wall paneling and furniture. It is hoped that this surfacing of plywood will eliminate or greatly reduce one of the main faults of plywood, face checking. Phenolic or melamine resins may be used for surfacing plywood since they are both outstanding in weather resistance. Comparative tests at Forest Products Laboratory and elsewhere have shown that melamine resins are unexcelled in outdoor durability.

It is also hoped that the use of resin-impregnated papers for surfacing plywood will eliminate the sanding operation. This not only saves the expense of the operation but, more important, saves an appreciable amount of wood since ¼-in. Douglas-fir plywood is now made by sanding 5/16-in. plywood.

Nevertheless, resin-paper-surfaced plywood will be more expensive than present plywood in spite of the elimination of the sanding operation, especially since, in most cases, both surfaces will receive the same treatment. This cost will, of course, vary widely depending not only on the cost of the resin and the paper, but also on the thickness of resin impregnated paper used. It has been estimated that the actual cost may vary from \$20 to \$90 per 1000 sq. ft. This

cost is based on surfacing both sides of the plywood with resin-impregnated paper, a necessary operation usually, both to ensure dimensional stability and to give equal protection to both sides. Where warping is not a problem, only one side of the plywood will be surfaced.

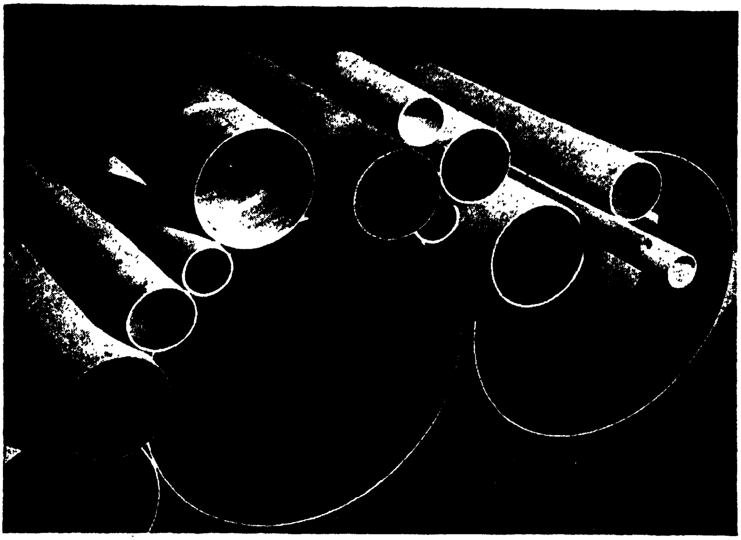
It is hoped that the plywood, as it comes from the press, will usually need no further treatment. In other words, the cost of painting or refinishing will be eliminated. It is entirely possible that this saving plus that resulting from the elimination of the sanding operation will equal the cost of surfacing plywood with resin-impregnated paper. Where refinishing is desired, it will probably be necessary to sand the surface before painting. Even so the painting cost should be less than that for ordinary plywood since fewer coats will be required.

This work is still in the development stage. Panels made on a 48 in. × 96 in. press will undoubtedly look different from panels made in a small laboratory press. It may develop that, in some cases, it will be preferable to impregnate the top veneer or to press the resin-impregnated paper on a thin, hardwood veneer at a higher pressure and subsequently glue this veneer to plywood. It will also be necessary to seal the edges of the plywood with a waterproof coating to prevent edge penetration of water.

Since the annual production of plywood is measured in billions of square feet and a rapidly increasing percentage is resin-bonded, it is evident that the potential market for resin-impregnated paper for surfacing plywood is large.

PLYWOOD TUBING

Plywood tubing was first produced commercially and in quantity early in 1942. Although the plywood industry experimented for many years to make tubing, it was not until the introduction of suitable plastics resin adhesives allowing sufficient slippage in molding that tubing manufacture became practical. At first this tubing was used only in masts for radio and radar installations. Because of its big advantage, a favorable critical strength-weight ratio, a 75-ft. plywood mast weighing 230 lb. replaced a metal mast weighing 1980 lb. Two miles of plywood sections, or enough for 150



Courtesy "Plastics World."

FIG. 33. Phenolic bonded plywood tubes are one of our strongest structural materials, pound for pound.

PHYSICAL PROPERTIES OF TYPICAL WELDWOOD TUBES AT 12% MOISTURE CONTENT*

Nominal Size, in.	Weight per Lin Ft	Moment of Inertia, psi	Radius of Gyration, in.
10 × ½	4.95	168.5	3.36
8 × ½	3.90	83.5	2.66
6 × ½	2.60	29.4	1.94
5¼ × ½	2.44	19.0	1.67
5 × ½	2.25	17.7	1.63
4 × ⅜	1.40	6.6	1.26
3 × ¼	0.78	2.2	0.96

MECHANICAL PROPERTIES — 5 MIN. DURATION

		At 12% Moisture Content	*At 5% Moisture Content*
Compressive strength (ultimate)	=	6,000 psi	8,750 psi
Modulus of elasticity	=	1,500,000 psi	1,720,000 psi
Modulus of rupture (bending)	=	12,000 psi	16,500 psi

* United States Plywood Corp.

75-ft. masts, can be loaded in a single trailer truck. Complete masts can be packed by the dozens in transport planes and flown anywhere.

Plywood pipe, because of its light weight, great strength and resistance to chemicals (improved by surface treatment with plastics or by treatment of the veneers before fabrication), can be used to carry liquids or gases. It will find wide acceptance as chemical pipe or under conditions that would quickly corrode metal. It will be used in remote places for irrigation and water supply where transportation and ease of handling are important considerations. The field for plywood tubing combined with plastics is as yet relatively unexplored, but as new applications are uncovered this business may assume the proportions of a major industry.

UREA TREATMENT OF WOOD

A new process for chemically treating wood has been announced by E. I. du Pont de Nemours & Company, Inc., and although it is still in the development stage, it may eventually prove of considerable importance. Chemically treated wood is supplementary to other new forms of wood that have been made possible by the application of synthetic resins to one of man's oldest materials. Among these are plywood, Impreg, Compreg and various combinations of wood with paper and other materials. The process is an indication that plastics are helping to improve the competitive position of some of the older materials, rather than displace them.

Wood is a material of prime usefulness that nature has provided in abundance and in easily accessible form, requiring neither mining nor drilling. With proper forest management and selective cutting, the supply of wood is constantly replenishable and inexhaustible. Some fifty species that are widely used for commercial purposes grow in the United States. Over a thousand others are not now used commercially. Each species produces woods of varying qualities, depending on where and how fast the tree grew, the grain of the wood and whether it is taken from the heart or from the sap section.

Wood as found in nature is not suitable for some uses. For many years, research workers have felt that if wood were improved in

certain respects, it would have more satisfactory application in many fields. The most desirable wood for some particular uses is now expensive, slow growing and not abundantly available. Fast-growing trees would be more actively cultivated if their wood could be endowed with the properties of the more desirable woods.

Wood has many virtues, but also, from the viewpoint of the engineer, fabricator, chemist, builder and user, many inherent defects. The limitations of wood must be known before it can be improved. Briefly, its failings are that it is slow drying; it checks, splits and warps during drying; it is flammable; it rots; insects eat it and bore holes in it; it is too soft for some purposes; it changes dimension with changes of humidity — swelling in damp weather, shrinking in dry weather and tending to warp in any weather; it is not waterproof; the grain raises; chemicals affect it; finishing operations are expensive and tedious; it is weak for certain purposes; it has little strength across the grain; woods having desirable color or grain may be too soft or weak for the uses for which their beauty might make them most desirable; and trees do not grow thick enough, tall enough or fast enough.

A number of the natural shortcomings of wood have been overcome. Modern kilns and accurate schedules dry wood rapidly. Chemicals, when applied to green wood, allow it to dry with little or no checking, splitting and warping, and at the same time allow the use of faster drying schedules. Wood can be made flameproof, rotproof, and less palatable to insects. The difficulty of trees not growing thick, tall and fast enough has been overcome through the development of some unusual resin adhesives. These make it possible to construct such large sections as beams, boat keels, arches and trusses from small, readily available, easily dried pieces of wood. These composite laminated items are much stronger, more durable and less expensive, and can be produced more rapidly than has been possible up to now.

There is still much room for the improvement of wood. The chemist and the engineer have only recently become aware of the possibilities. The lumberman carefully distinguishes between the different species and grades of wood but he tends to think of a board in the dealer's yard as his finished product. The chemist looks on wood

as a raw material, the properties of which may be altered to overcome its natural limitations. To him wood is primarily cellulose and lignin, and the varieties differ mainly in how these two substances are distributed and arranged; in other words, species differ structurally but are, chemically, quite similar.

The chemist has improved on nature through a new and outstanding development, the methylolurea treatment of wood. Methylolurea is used to designate dimethylolurea as well as the series of compounds resulting from the addition of varying amounts of urea to dimethylolurea. Urea has long been an article of commerce, but dimethylolurea has just recently become available on an industrial scale.

Many materials and processes have been considered for the impregnation of wood to minimize swelling, shrinking and warping and to improve its hardness and strength. Resins, partial resins, resin-forming chemicals, salts, sugars and a host of other chemicals, even gases, have been tried. Of all substances so far investigated, methylolurea has proved one of the most generally useful and practical.

Methylolurea can react with itself under certain conditions to form hard, water-insoluble, infusible resins. It can also react with the components of wood and alters the properties of wood when converted to resin within its structure.

When sufficiently treated, the wood loses its natural tendency to swell or shrink or warp with humidity changes, and the grain will not rise on wetting. The wood becomes markedly harder, stronger, stiffer and more durable. It can be highly polished and more smoothly worked. Its tendency to shred and splinter during sawing, planing, cutting and turning is reduced.

The natural color of wood is not altered by the treatment. However, suitable dyes can be introduced with the treating chemicals to color the wood throughout. For instance, a light-colored pine or poplar can be given the color of cherry, rosewood or mahogany, or colored brilliant red, green or purple. Freshly exposed surfaces can be finished without staining or matching, and scratched or marred surfaces can easily be restored by rubbing.

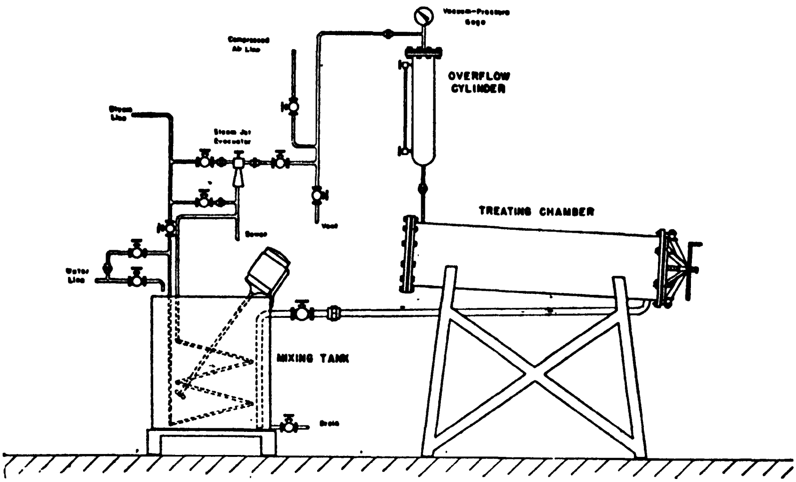
Actually the product is no longer wood; it is transmuted, to use

the term given it by du Pont, that is, transformed by methylolurea treatment to a product with properties fundamentally different from wood. Within the limits of possible impregnation, one species may be substituted for another or used for purposes for which it was not previously suitable. Thus, as is later more fully explained, available or lower cost woods, or woods having more favorable color or grain characteristics may be utilized and endowed with the properties required without the limit of natural characteristics. For instance, poplar can be made harder than hard maple. Soft maple or other close-grained woods may be used to replace dogwood or persimmon in textile shuttles. The compressive strength of wood as well as its hardness and resistance to the effects of moisture can be so increased that treated wood may be substituted for steel in certain textile machinery parts where wood has hitherto been unsuitable.

Methylolurea-treated, or transmuted, wood differs from untreated wood somewhat as steel differs from iron. As with steel compared with iron, treated wood may require slower rates of sawing, cutting and turning, different tool settings, harder tools or more frequent sharpening of tools than untreated wood.

Because of the increased hardness and density of treated wood, more power is required to drill holes and insert screws. However, the screw-holding strength is higher than that of untreated wood. Likewise, it is more difficult to drive nails into treated wood, but the nail-holding ability appears to be improved.

Methylolurea enters the wood structure as a water-soluble uncondensed material. In the course of drying, the methylolurea gradually reacts with itself and with the components of the wood, first to form insoluble but fusible products; with sufficient time or heat, the reaction is completed and an infusible product results. If the wood is subjected to sufficient heat and pressure while the resin is still in the fusible stage, the resin will melt, flow and allow the wood to compress. This treatment converts the resin to the final infusible form, maintaining the wood in the dimension resulting from the press. Thus treated wood may be compressed to produce a stable, extremely hard, dense product with a consolidated closed surface requiring no filling, sanding or polishing. It is possible to apply moderate pressures sufficient to compress and consolidate



Courtesy E. I. du Pont de Nemours & Co. Inc.

FIG. 34. This shows the arrangement of equipment used by du Pont in urea treatment of wood.

only the surface or outer zone of the treated wood to produce a finished, hard surface. Wood may thus be treated and then brought to the desired final dimension by heat and pressure. Polished or embossed platens may be used to reproduce polished or decorative finishes on the surface of the wood.

Treated veneers have increased strength and stiffness and may be used to form dimensionally stable plywoods that will resist checking, warping and splitting. Finished, highly polished, hard, mar-resistant surfaces may be produced directly by compressing the treated veneers under heated, polished platens.

When veneers are sufficiently impregnated and dried, they become self-bonding under the heat and pressure of the presses, and no other adhesive is required to form plywoods. The heat fuses the resin formed in the wood, and produces a hard, dense product.

The treatment apparently has no adverse effect on the gluing and finishing characteristics of the wood. Flame resistance is improved, and the wood is also more resistant to fungi, rot and pest infestation.

The process has promise in application to the sapwoods and heartwoods of many species. Sapwoods impregnate more easily

than heartwoods. The heartwood of most hardwoods is more readily impregnated than the heartwood of some softwoods.

The resin formed in the wood has no odor, is not toxic, is not affected by organic solvents or water, and as stated does not affect the color of the wood. The resistance of the treated wood to the action of most chemical agents is markedly improved.

It is also possible to impregnate sawdust, shavings or similar wood wastes and form them under heat and pressure into molded objects. Dyes or pigments may be included. The process is also applicable to other cellulosic and fibrous products such as paper, cotton, farm wastes, leather and the like. Bamboo and similar cane and fiber products can be treated.

APPLICATIONS. Investigations on production, procedures, properties and applications of methylolurea-treated wood are in progress. The process is just emerging from small-scale tests toward industrial evaluation and adaptation. Sufficient information has been developed to indicate that it is commercially practicable. The general procedure and limiting conditions have been established. The exact conditions for more effective treatment of specific items will necessarily have to be determined through plant tests and experience.

The methylolurea treatment of wood now appears to be applicable to almost all items manufactured from wood, from utility poles and structural timbers to pipe stems and parts for musical instruments. Fabricated articles such as veneers, flooring, furniture, boats, textile and other machinery parts, sports goods, pulleys, musical instruments, tool and knife handles, millwork, screen and door sash, rollers, wood heels, pencils, shoe lasts, tanks, sanitary ware, laundry equipment, chemical equipment, agricultural implement parts and many other items would be improved by the use of treated wood.

Low-cost woods, at present not suitable for many of the above uses, could be utilized. There are large quantities of woods available that are not widely used because they are too soft or too weak, crush or dent too easily, are not durable or present turning, working or finishing difficulties. Such woods as soft maple, tupelo gum, yellow poplar, a number of the pines and other woods can be treated

and their usefulness greatly extended. They could release hard maple, oak, walnut and other more desirable, less available and more expensive woods for other more essential uses. In turn, these woods can be further improved. Soft maple can be made harder than hard maple, and hard maple can be made harder than ebony, which is the hardest well-known wood. Industry can thus now create in a few days woods harder than ebony, which nature takes centuries to grow.

Veneers, furniture, flooring, castings, stair treads, doors, trays, office, boat and store equipment and cabinet work are some items for which wood may now be chosen for color and beauty of grain, more or less regardless of its other properties. Thus, tidewater red cypress with its attractive grain, California redwood with its satin-like texture and warm red color, and almost white cottonwood matching the best bleached woods are but a few examples of the many woods that may now compete with other species. Advantage can now be taken of their natural beauty, unencumbered by inherent defects that have heretofore limited their use. Hardness, finish, strength, density and durability can be added by the treatment. New furniture and even floors can now be made of beautiful woods, woods that could not be used for furniture or floors before. They will be difficult to mar and readily restored if damaged.

Doors, windows and drawers can be constructed to close dimensions and will not stick or become loose with changes in atmospheric conditions. Furniture can be shipped to the humid tropics or to dry Arizona with the assurance that drawers and doors will operate smoothly and remain as close fitting in one place as the other. Since the treatment imparts dimensional stability and allows smoother, cleaner and more accurate machining, furniture and other items manufactured from wood could be assembled from finished standardized wood parts, eliminating costly and laborious fitting by hand.

Perhaps boats can be built with hulls that will not leak after drying and will not require recaulking or frequent painting, with decks that retain their finish and resist the action of the elements, and with cabins and furnishings of less costly available woods having

properties superior to those of the imported and scarcer woods now so widely used.

Because of greater strength and stiffness, lighter construction of some items is possible, representing a saving in wood that will offset part of the cost of treatment.

Emphasis has been given to the complete impregnation of wood to obtain the maximum freedom from dimensional changes. Under some conditions, however, complete impregnation is not necessary, desirable or economically feasible, and a shallow or perhaps even a surface treatment may contribute the necessary improvements. The complete impregnation of wood, while increasing the compressive, tensile and bending strength, tends to lower the impact strength or resistance to shock. It becomes more brittle, just as hardened steel is usually more brittle than soft steel. As it is often desirable to caseharden steel, leaving a softer, tougher core to withstand impact, so some wood members may be given a treatment to harden and strengthen the outer zone, leaving the untreated inner fibers in a more resilient flexible state to withstand impact stresses.

Timbers and wood members required for the construction of trestles, towers, homes, various buildings, boats, airplanes and the like may be improved by a hardened, high-strength shell that would enable the wood to take much higher loads or allow the use of lighter construction. The treatment of the outer zone would also contribute improved dimensional stability, flame resistance and resistance to decay and insect infestation. Partial impregnation could be used for construction lumber, piling, utility poles and the like for which complete impregnation would not be economically practicable.

When a hard consolidated surface on wood is needed and dimensional stability is not essential, the treatment may be applied to the surface by diffusion or other means and the treated wood may be subjected to heat and pressure. This would be applicable to the production of hard-surfaced flooring or to improving the dent and mar resistance of furniture and paneling.

The Process. The impregnation of wood with resin-forming methylolurea and the conversion of this chemical to resin within

the wood is relatively simple and inexpensive, involving no new procedures or new or special equipment.

A water solution of an uncondensed methylolurea is forced into the wood structure. The methylolurea is there converted to resin by the natural acids present in the wood. Heat such as that used in normal kiln drying speeds the conversion of the methylolurea in the wood to water-insoluble resins. The process takes place with sufficient rapidity at normal temperatures to be completed in the usual air-drying period. A permanent resin that is both hard and insoluble is developed within the wood structure either at normal or at kiln temperatures. If the kiln drying has not been at too high a temperature or if it is conducted rapidly enough, the resinification reaction will proceed to the insoluble but still fusible stage and will remain so for a period of time. If wood so dried is heated to 240°F. or higher, the resin fuses and will flow under pressure and the resinification is rapidly completed to the infusible state. The wood will retain permanently the dimension and surface produced by the compression.

The solution may be impregnated into wood by various means. One of the most effective commercial procedures for impregnating wood uniformly is the so-called "full cell" or vacuum-pressure impregnation process. The wood is placed in a chamber and the air withdrawn. The treating solution is then introduced into the evacuated impregnating chamber in sufficient quantity to cover the wood and allow for the volume of solution that will be absorbed. The chamber is then opened to the atmosphere, or air pressure applied. After a determined period the solution is drained off and the wood removed for drying. For small items, centrifugal impregnation may be practical.

The wood that is to be treated should for most purposes be dry or at least dried below its fiber-saturation point. When the methylolurea solution is forced into the wood, it first enters the cell cavities. Then it rapidly diffuses into the cell walls, where, under the influence of the acids of the wood, it begins to polymerize and become an insoluble resin. If wood is green, the cell cavities are partly full of "free" water and the fibers are saturated. When the methylolurea enters the cell, its rate of diffusion into the cell walls is im-

paired, and it may convert to the insoluble form before it has an opportunity to soak into the cell walls.

The concentration of the methylolurea in the solution, the particular methylolurea used (that is, the proportion of urea to dimethylolurea), the temperature, what pressure, if any, is applied, and the length of each phase of the treating cycle are conditions that depend on the nature of the item being treated, its dimension and species, whether of sapwood or heartwood, what degree of treatment is necessary, and what final properties are required.

The vacuum-pressure treatment involves the following steps:

1. Place the wood in the treating cylinder.
2. Apply vacuum for the required period.
3. Introduce the solution without releasing the vacuum until the wood is completely submerged and the solution is in the overflow tank.
4. Apply pressure for the required period.
5. Discharge solution into reservoir for reuse and remove wood.
6. Dry the wood.

For most veneers, up to 1/16 in., it is not usually necessary to apply pressures above atmospheric to obtain adequate absorption. For deep penetration of lumber, pressures of 50 to 100 lb. or more per sq. in. are required. For sapwood of both softwoods and hardwoods and the heartwoods of some hardwoods, an impregnation cycle of 20 to 50 min. vacuum (26 to 28 in.) followed by 100 lb. per sq. in. pressure applied for 10 to 50 min. at room temperatures, is usually sufficient.

To conserve chemicals, increase the capacity of the treating unit, and reduce impregnation time, it is preferable that the wood article be cut to almost its final form prior to treatment. The items to be treated need not be separated or spaced but may be bulk-piled in the treating chamber or loaded in bundles, even in baskets, if small items are being considered. During the treating operation, the wood will expand. Allowance should be made for this expansion in loading the cylinder with the wood.

THE EQUIPMENT. The equipment required may be quite simple. It can be of the same type as that now used in treating lumber with

creosote and flameproofing chemicals, though smaller scale equipment may be used because of shorter treating cycles. For test purposes or small-scale operations, it can usually be assembled from equipment at hand in most plants. All that is required is a chamber capable of withstanding the necessary vacuum and pressure, in which the wood is placed. A steam jet ejector is an effective simple means of producing the necessary vacuum. It should be equipped with a pressure door or removable head and a source of vacuum and of pressure. A tank for preparing the solution, an auxiliary overflow tank, and means for drying the wood are also needed. Mild steel equipment may be used. The chemicals are no more corrosive than water and are neither flammable nor toxic. To prevent rusting and possible discoloration of the wood, a waterproof finish should be applied to the exposed surfaces of the equipment.

THE CHEMICALS. A water solution of an uncondensed methylolurea is employed. This may be obtained by reacting urea and formaldehyde in the proper proportions and under controlled conditions. However, a simpler, more economical and convenient method of preparing the solution is merely to dissolve urea and dimethylolurea (or, for brevity, DMU) in water in the required proportions. Both materials are white water-soluble solids. They are produced from ammonia, carbon dioxide and methanol, which are synthesized from coal, air and water. Urea results from the reaction of ammonia and carbon dioxide. Formaldehyde, which is derived from methanol, condenses with urea to form DMU.

The proportions required will depend somewhat on the nature of the item being treated and the results desired. For most purposes a solution of 1 to 2 parts of urea and 6 parts of DMU dissolved in 20 to 24 parts of water is satisfactory.

A solution of 1 part urea to 3 parts of DMU is prepared by dissolving 30 lb. of urea and 100 lb. of commercial DMU (equivalent to 90 lb. of dry DMU) in 350 lb. or 42 gal. of water. This will result in 53 gal. of solution. The solution should be prepared in a tank equipped with a steam coil and a stirrer to effect rapid solution. The solids are added and the solution heated to 130° to 150°F. during its preparation.

Methylolurea solutions are highly reactive, as evidenced by the

reactions that ensue when they are impregnated into wood. Certain precautions are therefore necessary to prolong their usefulness and prevent spoilage. If the solution is to be stored for more than 8 hr., it is important that it be maintained mildly alkaline, at *p*H of about 8.0. When freshly prepared from urea and commercial DMU, the solution will have approximately the desired alkalinity. When wood is impregnated with this solution, wood acids are extracted and the solution tends to become acidic. In operation, the solution may be allowed to become slightly acid (*p*H not less than 6.0) if promptly neutralized with alkali, avoiding an excess (*p*H not above 9.0). The acidity of the solution can be readily controlled by the use of special test papers. If the solution is to be stored, the cooler it is kept, the longer it will last.

If the wood is to be colored by the treatment, water-soluble dyestuffs are added to the treating solution. The color produced by the dye is apparently not affected by the methylolurea. The dyes selected should have a neutral or slightly alkaline reaction in solution.

Both urea and DMU are commercially available and inexpensive chemicals now being produced on a large scale.

Urea, also known as carbamide, is a white crystalline, water-soluble, odorless product resembling granulated sugar in appearance. It is widely used in fertilizers, plastics, plywood adhesives, pharmaceuticals, animal feeding and for many other purposes.

Dimethylolurea, or DMU, is a chalky-white solid slowly soluble in cold water but rapidly dissolved by hot water. It gradually becomes less soluble on storage, particularly in hot weather, and should be obtained as required.

Costs. Fundamentally, the costs of the methylolurea treatment of wood are low. The cost of the chemicals, operation charges, and investment in equipment is moderate and in many instances may be more than balanced by the resulting advantages and economies. Some of these are:

1. When veneer, which is valued on its surface area, is treated, it remains close to its green dimension, representing a gain of 5 to 10 per cent in area over untreated veneer.

2. Because of greater strength and stiffness, lighter construction or less wood is required for certain items.
3. Low cost, readily available woods can be treated and made competitive to higher priced scarcer woods that may have the added cost of transportation from far places.
4. Wood may be used for purposes for which it is now not suitable and is therefore in direct competition with more expensive plastics and metals.
5. Finishes and colors can be produced directly on wood by pressing, eliminating such expensive and time-consuming operations as filling, sanding, staining, rubbing, varnishing and polishing.
6. Furniture, drawers, doors and the like can be made to fit and operate freely under varying atmospheric conditions, resulting in economies in production as well as in servicing.
7. Since the finish produced is "built-in," surfaces that are scratched or dented can be readily restored by smoothing and rubbing, requiring no matching, filling, varnishing or refinishing, an important item of cost in furniture handling.
8. Certain manufactured items can be compressed to final size, in one step eliminating machining costs and applying a surface finish. This may be applicable to flooring, table and desk tops, furniture items, machine parts, rules, levels and the like.
9. Increased durability or resistance to water, chemicals and solvents can be translated into longer life and less replacement for such items as laundry and chemical plant equipment, wood tanks, window, screen and door sash and machine parts.
10. In production of plywood or laminated veneer construction, the treated wood is self-bonding, eliminating the need for other adhesives.

The direct costs depend on a number of factors such as the scale of operation. The cost of chemicals varies with the amount used, which depends on the type of lumber or item being considered and the purpose of the treatment since this determines whether the

wood is to be fully or partially impregnated. Commercial woods grown in the United States vary in weight from about 24 to 47 lb. per cu. ft. Exclusive of timbers, structural parts and other items that would be only surface or case-impregnated, the application of chemical varies from 10 to 30 per cent of the dry weight of the wood. Thus, from 2.5 to 14 lb. per cu. ft. of wood may be required. For average requirements, applications of 15 to 20 per cent would suffice. This represents a dosage of about 5 to 6 lb. of methylolurea for the average wood weighing about 30 lb. per cu. ft. The present cost of the chemicals is 8 to 9 c. per lb. at the mill in small quantities. Thus, the cost of chemicals for the complete impregnation is of the order of $0.035 to $0.045 per bd. ft. of lumber. For the average veneer, this cost is about $0.0015 per sq. ft.

When the treatment is to be limited to the outer zone of the wood, applications of from ½ to 3 lb. of chemical per cu. ft. would be considered. This "case hardening" treatment would represent a chemical cost of from $0.003 to $0.02 per bd. ft.

The treating installation involves no new type of equipment. The procedure and the costs of treating equipment and its operation are well known in the wood-treating industry. Simple, easily operatable units can be installed at relatively low costs for the treatment of small items. The short treating schedules allow large production from equipment of relatively small size.

The development of methylolurea impregnation of wood means in essence that it is now practical and feasible for wood to be remade — engineered to specifications of service and appearance. The shackles of unalterable properties and of limitations to certain species can now be cast aside. The new substance, transmuted wood, that is, made from wood and looking like wood, can successfully compete with plastics and metals that for several years gradually have been pushing wood into the discard for many purposes. Plastics and metals were fashioned to the conditions demanded of them, even to looking like wood. Now wood can be formulated for greater interchangeability and to achieve fields of usefulness extending well beyond the frontiers to which it has hitherto been limited. The lumber industry now faces its greatest opportunities along with its greatest competition. It has several new and potent weapons.

GORDON AEROLITE

Gordon Aerolite, developed by Dr. N. A. de Bruyne of Aero Research Ltd., consists of phenol-formaldehyde resin with unwoven linen filler. The flax fibers are not crimped and only very slightly twisted, but in general form and appearance the material is similar to laminated sheet. Some of the properties of this material are given in Table III in comparison with stainless steel and aluminum alloy and show that the strength-weight value of Gordon Aerolite in one direction is higher than aluminum alloy or high-tensile steel.

TABLE III. PROPERTIES OF SHEET CONTAINING UNIAXIAL FLAX FIBERS COMPARED WITH STEEL AND ALUMINUM ALLOY

Resin content, approximately 25%

	Gordon Aerolite	Stainless Steel	Aluminum Alloy
Density, gm per cu cm	1.47	7.85	2.8
Tensile strength parallel to laminations,			
Tons per sq in.	30	80	30
Kilometers	32	16	17
Compressive strength, ton per sq in.:			
Parallel to fibers	13		
At 90° to fibers	6.2		
Shear strength parallel to fibers,			
Tons per sq in.	2.45	50	18
Kilometers	2.62	10.1	10.1
Young's modulus, psi	7×10^6	30×10^6	10×10^6
Kilometers	3330	2680	2540

CHAPTER IX

Synthetic Rubbers

CLASSIFICATION OF SYNTHETIC RUBBERS

Type	*Trade Variety*
1. Diolefin (butadiene and isoprene polymers)	Natural Rubber (isoprene) Buna (German) Methyl Rubber (German) SKA (Russian, from petroleum) SKB (Russian, from alcohol)
2. Chloroprene (from acetylene)	Neoprene (du Pont) Sovprene (Russian)
3. Diolefin (polymerized with modifiers)	Buna S (Goodyear, Goodrich, Firestone, U. S. Rubber) Perbunan (Buna N) (Standard Oil) Ameripol (Goodrich) Chemigum (Goodyear)
4. Diolefin (polymerized with an olefin)	Butyl (Standard Oil)
5. Polysulfide	Thiokol (Dow, Thiokol Corp.)
6. Rubber-like materials (non-vulcanizing)	Vistanex (Standard Oil) polybutenes Koroseal (Goodrich) Vinylite (Carbide)

Buna S is made from butadiene + styrene.
Perbunan (Buna N) is made from butadiene + acrylonitrile.

SYNTHETIC RUBBERS NOW PRODUCED IN THE UNITED STATES

BUNA S (GR—S): COPOLYMERIZED BUTADIENE AND STYRENE.

Structure. $(-CH_2-CH{=}CH-CH_2)_x(-CH_2-CHC_6H_5)_y$.

Status of Manufacture. Principal synthetic rubber produced under government program. Was made and used in large quantities in Germany since 1936 as a general substitute for rubber, particularly in tires. Manufactured in government plants under control by rubber companies.

Method of Synthesis. Copolymerization in aqueous emulsion.

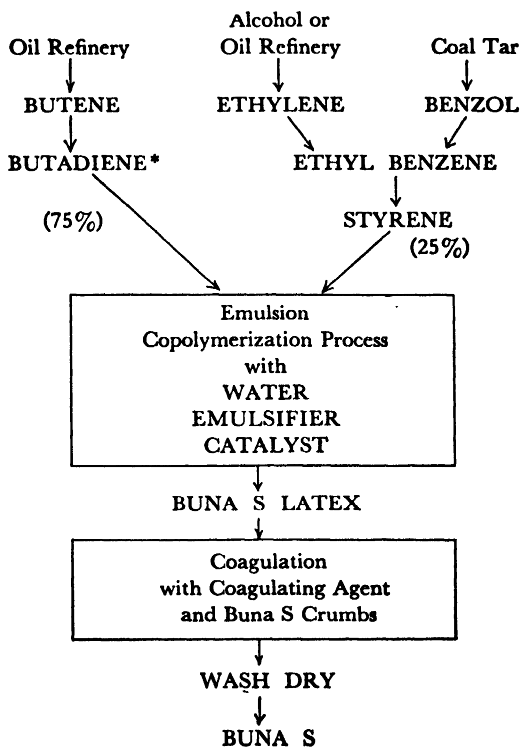
Vulcanizing and Processing. Vulcanizing and processing are similar

to the processes for natural rubber. Greater power requirements for plasticization than natural rubber.

PROPERTIES AND USES. In general, the properties of Buna S are similar to those of natural rubber and its swelling characteristics in gasoline and mineral oil are but little better than those of natural rubber. Water absorption is only 65 per cent of natural rubber, and aging qualities, although affected by temperature, are considered superior, these last-named qualities making it useful for cable coverings.

HOW BUNA S IS MADE

This is a "batch" process as against a "continuous" process such as used in making butyl.



*Also can be produced from acetylene, natural gas or alcohol made from grain or potato, or almost any starchy vegetable material or refinery gas.

Comparison of Buna S with Natural Rubber for Tires. Any attempt to evaluate Buna S in terms of natural rubber must be qualified by the statement that Buna S is now the subject of intensive research and experiment. New discoveries are constantly being made to improve its manufacture, compounding and processing into finished products.

Advantages. Buna S, like natural rubber, can be vulcanized with sulfur and rubber accelerators. It can be processed on the same machines. It can be reclaimed. Its resistance to atmospheric deterioration is slightly higher than natural rubber. Buna S passenger-car tires and small truck tires are proving eminently satisfactory.

Disadvantages. At the present time, Buna S requires slightly more milling. It is less sticky and plies must still be cemented with natural rubber. In some cases, it must be cooled after curing before handling to avoid tearing. It has less stretch than natural rubber. Buna S tubes have less tensile strength than natural rubber tubes, and a 6:00–16 size Buna S tube may weigh about 1 lb. more than a natural rubber tube because it is made thicker.

PERBUNAN (FORMERLY BUNA N): COPOLYMERIZED BUTADIENE AND ACRYLONITRILE.

Structure. $(—(CH_2—CH{=}CH—CH_2)_x—CH_2—CHC{\equiv}N—)_y$.

Status of Manufacture. First made in Germany about 1935 by I. G. Farbenindustrie. Now made in this country by Standard Oil Co. (N. J.).

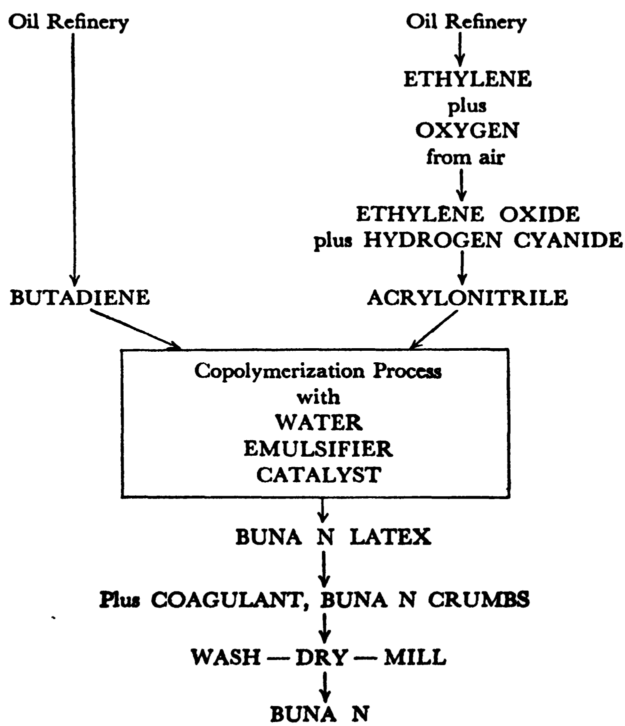
Method of Synthesis. Copolymerization of butadiene and acrylonitrile in aqueous emulsion.

Vulcanizing and Processing. Vulcanizing same as for natural rubber, using sulfur and same types of acceleration. In processing, like Buna S (GR—S), it cannot be plasticized as easily as natural rubber. Softeners are desirable to increase elasticity, tack and assist in extruding. Addition of natural rubber or reclaimed natural rubber improves working qualities. Is much tougher and more difficult to process than natural rubber. It generates more heat in milling, is less thermoplastic, but has a tendency to harden after long periods at high temperatures.

PROPERTIES AND USES. Primary property is its resistance to gasoline and other aliphatic hydrocarbons. Swells in aromatic and chlorinated hydrocarbons such as benzol, toluol, solvent naphtha, di- and trichloroethylene and in certain ketones. Aging qualities and resistance to ozone said to be superior to those of natural rubber but elasticity, rebound and electrical properties poorer; because of the last named not being used as electrical insulation. In heat and abrasion resistance it surpasses natural rubber and is less than half as permeable to air and gases.

Finds greatest use where its oil-resistant qualities are needed, as in packing rings, gaskets, printing rolls, gasoline hose, hose for spraying paint, cable covers and conveyor belts. Has also been used in bulletproof tanks. Although Perbunan tread compounds are said

HOW PERBUNAN (BUNA N) IS MADE



to be equal or superior to the best rubber tread compounds, its use in tires is not of commercial importance, as other synthetics easier to process and fabricate are considered more economically suitable.

HYCAR O R (AMERIPOL): BUTADIENE COPOLYMER.

Structure. A copolymer of butadiene and acrylonitrile similar to Perbunan. Two types made.

Status of Manufacture. Date announced, 1940. Made by Hydrocarbon Chemical & Research Co. (Hycar Chemical); owned jointly by Phillips Petroleum Co. and B. F. Goodrich Co. Plant of 2000 long tons capacity constructed in 1940.

Method of Synthesis. Polymerized under pressure in emulsion with soap and water. The butadiene is obtained from petroleum; source or nature of copolymer not announced.

Vulcanizing and Processing. Vulcanizing similar to natural rubber, except that less sulfur and more accelerator is required. Is tough and does not break down on a mill to the extent natural rubber does, and more softener is required. Pigments have the same relative effect as with rubber.

PROPERTIES AND USES. Two distinct types of butadiene copolymer synthetic rubber are said to be made. One is a rubber suitable for tire manufacture and the other a special oil-resistant rubber.

Properties such as tensile strength and elasticity are said to vary over a wide range, according to method of compounding. Maximum tensile strength obtained with channel black loading. A tensile strength up to 4000 lb. and 600 per cent elongation may be obtained. Good heat and abrasion resistance claimed and superior resistance to mineral, animal and vegetable oils and fats, to oxidizing effects of metallic soaps used as driers in paints and inks, to all petroleum products and to benzene, alcohol, water and carbon tetrachloride, although badly swollen by acetone.

Aging resistance is superior to that of natural rubber and resistance to alkalies and acids about the same. Elasticity, tear resistance and rebound lower than for similarly compounded natural rubber. Hardness may be varied over a wide range. Becomes stiffer than natural rubber at subfreezing temperatures but is said to be still flexible at −50°C. Resistance to oxidation and decomposition

when exposed to heat said to be excellent and permeability to air and gases less than natural rubber.

Oil-resistant products of Ameripol include gasoline hose, automobile and airplane parts, packing joints and valves, linings for bulletproof gasoline tanks, printing rollers and the like. Tires are said to be slightly superior to tires made of natural rubber compounds in abrasive resistance and far superior in the presence of oils and high temperature.

CHEMIGUM: BUTADIENE COPOLYMER.

Structure. Not announced but said to be a copolymer of butadiene and acrylonitrile similar to Perbunan.

Status of Manufacture. Announced in 1940 by Goodyear Tire & Rubber Co.

Method of Synthesis. Announced as derived from petroleum through a cracking process.

Vulcanizing and Processing. Vulcanizing similar to natural rubber. Said to process more easily than Buna on equipment and by methods used for natural rubber. Tends to be soft and plastic when warm and mixes well with natural rubber.

PROPERTIES AND USES. Specific gravity 1.06. A Buna-type product resembling in physical appearance grade of rubber known as brown crepe. Is tough and equal or superior to natural rubber in strength and resistance to aging and sunlight. Much less soluble in conventional rubber solvents than natural rubber and its oil resistance makes it suitable for gasoline hose and similar uses. Tires made of Chemigum are said to be very satisfactory.

NEOPRENE (FORMERLY DUPRENE): POLYMERIZED CHLOROPRENE.

Structure. $(-CH_2-C\,Cl{=}CH-CH_2-)_x$.

Status of Manufacture. Date announced 1931. Made by E. I. du Pont de Nemours & Company, Inc.

Method of Synthesis. Polymerization of chloroprene in emulsion under carefully controlled conditions.

Vulcanizing and Processing. Vulcanized by heat alone, but quality of vulcanized products is improved by the use of metallic oxides as vulcanization aids. Processed like natural rubber.

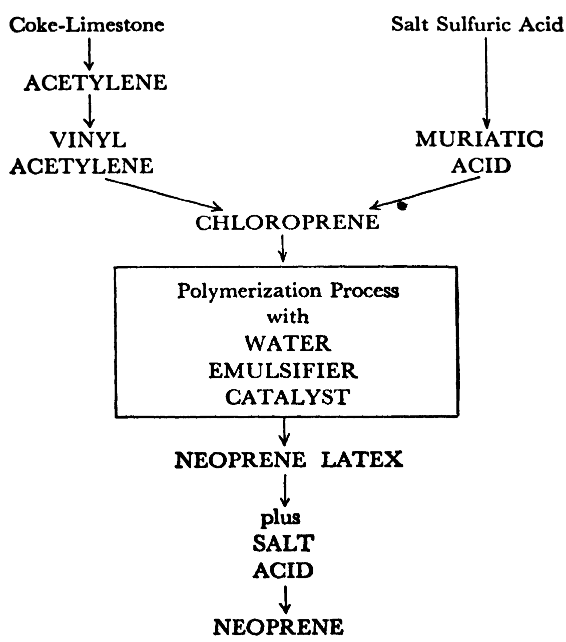
PROPERTIES AND USES. The physical qualities of Neoprene, made

in several types, may be modified over a wide range by the proper choice of pigments, accelerators, anti-oxidants, etc. The unvulcanized product is a plastic with considerable elasticity, like unvulcanized rubber. It is thermoplastic and formed, like rubber, by calendering, extruding and molding at high temperatures.

The vulcanized Neoprene is resistant to oils and, although virtually all animal, vegetable or mineral oils cause it to swell somewhat, it usually retains its properties better than rubber. It is slightly less elastic than rubber but is more heat-resistant and resists sunlight better. Loss of properties on freezing is greater than with rubber unless oil-soaked or specially compounded. Type FR, introduced recently, is said to be exceptionally immune to the effect of subzero temperatures.

The specific heat (0.52) of Neoprene is the same as for rubber. It has approximately the same tensile strength as similarly compounded rubber. The abrasion resistance of tire treads is about

HOW NEOPRENE IS MADE



equal to that of the best rubber tire tread compounds. Neoprene has about equal abrasion resistance to natural rubber when dry but is many times more resistant after having been soaked in oil.

Used for tank linings, reaction vessels, conveyor belts, gaskets, hose for oils, solvents and gases such as chlorine, clothing for acid protection, laboratory tubing and similar purposes.

VISTANEX: POLYMERIZED ISOBUTYLENE.

Structure. $(\text{—}CH_2\text{—}C(CH_3)_2\text{—})_x$.

Status of Manufacture. Date announced, 1937. Made by Standard Oil Co. (N. J.) and marketed by Advance Solvents & Chemical Corp. and Moore & Munger Co.

Method of Synthesis. Isobutylene derived from cracking of petroleum is polymerized at low temperatures with catalysts of an acidic nature, such as titanium tetrachloride, boron fluoride and aluminum chloride.

Vulcanizing and Processing. Cannot be vulcanized. Less thermoplastic and the degradation or breakdown by mechanical milling or mixing is less than for natural rubber. It may be compounded with natural rubber in certain proportions to give a curable product useful in steam hose, conveyor-belt covers, cable coverings and other products resistant to aging or chemical action.

PROPERTIES AND USES. Possesses unique qualities owing to its lack of unsaturation. Exhibits extreme resistance to ozone, acids, alkalies and corrosive salts and has excellent aging properties, particularly at high temperatures. Its water-absorption and vapor-permeability properties are extremely low. It is resistant to most vegetable and animal fats, oils and greases, and is insoluble in alcohols, esters, ketones and most organic solvents containing oxygen; but is soluble in petroleum and coal-tar solvents and in some chlorinated solvents. Used in the manufacture of cable sheathing, acid-resistant linings, electrical insulation, adhesives, artificial leather and like products.

BUTYL RUBBER (GRI): COPOLYMER OF A BUTENE AND A DIOLEFIN.

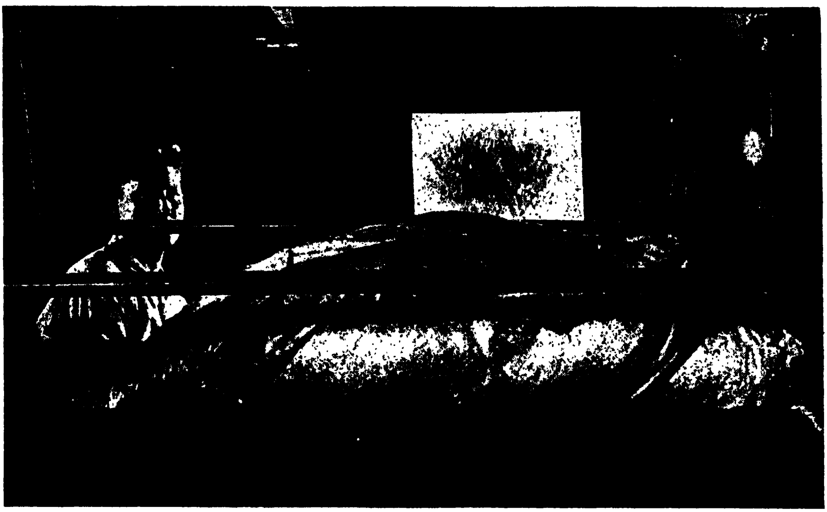
Structure. $(\text{—}CH_2C(CH_3)_2\text{—})_x(\text{—}CH_2\text{—}CH{=}CH\text{—}CH_2\text{—})_y$.

Status of Manufacture. Made by Standard Oil Co. (N. J.); date announced, 1940.

Method of Synthesis. Produced by low-temperature copolymerization of isobutylene and a small amount of butadiene or other diolefin, such as isoprene. The isobutylene is procured from petroleum by cracking, isoprene from petroleum or turpentine.

Vulcanizing and Processing. Vulcanizes like natural rubber. Processed like natural rubber or conventional rubber machinery. No breakdown period necessary.

PROPERTIES AND USES. Butyl rubber regarded as outstanding in that it possesses only 1 or 2 per cent of the available unsaturation of



Courtesy Standard Oil Co. (N. J.)

FIG. 35. Synthetic rubber is worked between large steel rolls. This shows production of butyl rubber.

natural rubber, just enough for vulcanization. This quality gives it unusual properties in aging resistance and stability in the presence of ozone. Swells like natural rubber in petroleum and coal-tar solvents but does not swell in most vegetable and animal fats and oils. Resistant to acids, including sulfuric and nitric, it has low water absorption, high heat resistance, excellent flex resistance, and is highly impermeable to air and gases, such as hydrogen, helium and carbon dioxide. Its rebound is low at room temperature but high

at high temperatures. The general range of molecular weight is 40,000 to 80,000 and specific gravity is 0.91.

Said to be very satisfactory for inner tubes in that it holds air longer than natural rubber. Tires have shown a life about 50 per cent of natural rubber tires at speeds under 40 miles per hr. Electrical properties make it outstanding for cable insulation. Used also in fire and steam hose, molded goods, proofed goods, tank linings, conveyor belts and in general replacement of natural rubber.

HOW BUTYL IS MADE

This is a "continuous" process as against a "batch" process as used in making Buna.

Oil Refinery ↓ ISOBUTYLENE (95–98%)

Oil Refinery ↓ BUTADIENE or Turpentine ↓ ISOPRENE (or other diolefin) (2–5%)

↓

Polymerization Process with CATALYST

↓

BUTYL RUBBER CRUMBS

↓

WASH—DRY—MILL

↓

BUTYL RUBBER

THIOKOL: ORGANIC POLYSULFIDE.

Structure. $(-R-\underset{\underset{S}{\|}}{S}-\underset{\underset{S}{\|}}{S}-)$ where R is an organic radical such as $(-CH_2-CH_2-)$ or $(-CH_2-CH_2-O-CH_2-CH_2)$, depending on aliphatic dihalide used.

Status of Manufacture. First announced in 1932. Manufactured by Thiokol Corp. and Dow Chemical Co. Made in several grades and types. Annual production of all types 3000 tons.

Method of Synthesis. Reaction between organic dihalide and alkali polysulfide. Raw materials used are dependent on type; ethylene dichloride and sodium tetrasulfide give Thiokol A. The organic compounds, which may be obtained from petroleum products, are chlorinated by chlorine obtained from salt. The sulfides are made from sulfur and alkali.

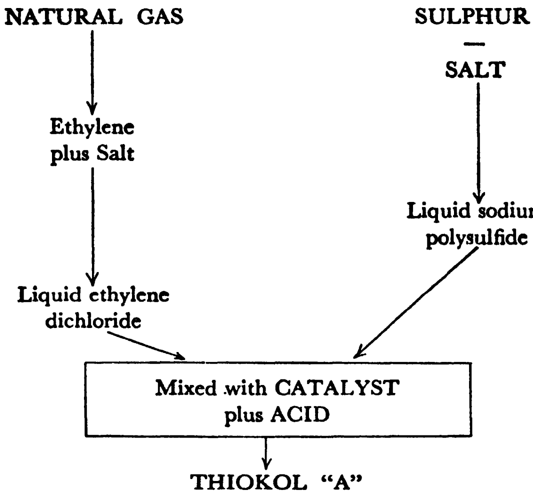
Vulcanizing and Processing. Vulcanizes with metallic oxides, sulfur being used as an accelerator. Processed on regular rubber machinery by special methods. Is frequently mixed with natural rubber. Reinforcing pigments and modifying agents are added, as with natural rubber.

PROPERTIES AND USES. Thiokol is made in several types, from several primary materials. A variety of products, some of which are rubber-like, can be made by varying the kind of polysulfide and hydrocarbon. Some of the products are used in the plastics industry and some as a rubber substitute. The ethylene polysulfides are virtually inert to all organic solvents, including benzol, toluol, xylol, carbon tetrachloride, lacquers and lacquer thinners, acetone, water, salt solutions, dilute phenol, sulfuric acid, hydrochloric acid and acetic acid; whereas other types are resistant to petroleum but swell to varying degrees in certain chlorinated and aromatic hydrocarbons. They show excellent resistance to ozone, oxygen and sunlight but are relatively low in tensile strength, and heat and abrasion resistance.

They burn slowly and have poor electrical properties compared with natural rubbers but good enough for low-voltage insulation. They are not recommended for use at extreme temperatures, as they harden at sub-zero temperatures and are subject to plastic flow at temperatures slightly above atmospheric. They are highly impermeable and are apparently the most resistant of all the synthetic rubbers to gasoline, benzene and oil.

Thiokol is not suitable for tire treads, although a new type (H) is said to be suitable for recapping. Used in the automotive industry for coating paper gaskets and also in the manufacture of gasoline and paint-spray, hose, printers' blankets, rubber printing plates and cable coverings.

HOW THIOKOL IS MADE



AGRIPOL (NOREPOL): A CHEMURGIC PRODUCT MADE FROM SOYBEAN OIL. Developed by Northern Regional Research Laboratory.

Status of Manufacture. First announced late in 1942, by the manufacturer, Reichhold Chemicals, Inc., Detroit.

Method of Synthesis. Polymerization of fatty acids and ethylene glycol. The fatty acids are secured by extraction from soybean oil.

Vulcanizing and Processing. Vulcanizing about the same as for natural rubber. Can be worked and formed in existing rubber equipment and compounded with customary fillers used with natural rubber.

PROPERTIES AND USES. Announced as inferior to natural rubber in tensile strength and resistance to severe abrasion, hence not suitable for tires. Said to be equivalent to natural rubber in flexibility at low temperatures and superior in aging and resistance to oxidation.

PARACON.

Paracon is an interesting new type of synthetic rubber for specialty uses developed by the Bell Telephone Laboratories as a result of peacetime research on insulating materials. It is of the polyester

type and similar to Norepol but excels in many properties.

An important advantage of Paracon is that it can be synthesized from a variety of basic raw materials — oil, vegetable, etc. It therefore does not compete with other synthetic rubbers for its raw materials. Although many types of Paracon are theoretically possible, availability and cost of new materials and difficulty of manufacture limit the number of useful products.

In its raw state, Paracon is quite plastic but can be worked on conventional rubber machinery. If fillers are added at the start of milling the uncompounded polymer will be less tacky. The oxide pigments are best for this purpose. Carbon black is not necessary with Paracon, as it is with the Buna-type synthetics, and, since it has some effect on the curing rate, its use is not advisable.

Unlike natural and other synthetic rubber compounding, Paracon vulcanization is accomplished without sulfur and accelerators. Paracon is well suited for use in gaskets, hose, etc., for molding into intricate shapes and for use in the manufacture of rubberized fabrics.

Physical properties of the vulcanizates vary according to the formulation. However, in general a tensile strength of 1500 to 2500 lb. per sq. in., elongation of 400 to 600 per cent, and a tear resistance better than most Buna compounds are obtained. Paracon has exceptional heat resistance, and compounds in service at 302°F. outlast both natural and synthetic rubber. It also has good resistance to oil and gasoline. It is equal to the Buna type of synthetic rubbers and therefore superior to natural rubber in rate of aging in air and oxygen.

Paracon has no advantage over Norepol in flex resistance and is inferior to natural rubber in resistance to steam, alkalies and acids.

The synthesis of Paracon was accomplished by C. S. Fuller, B. S. Biggs and their associates of Bell Telephone Laboratories. The laboratories turned over to some chemical manufacturing companies full information on the processes involved in order to carry the development from the laboratory scale to that of commercial production. One of the companies now producing Paracon on a semicommercial scale is The Resinous Products & Chemical Company.

PARAPLEX X-100.

The first Paracon type elastomer to be produced in a pilot-plant scale is Paraplex X-100.* It is the newest of the Paraplex series, alkyd resins that have long been used for plasticizing different types of finishes, notably nitrocellulose lacquers. In composition and general properties the new resin is closely allied to the other Paraplex resins, but its greatest utility will probably be in new and different applications. Unlike the others in this group, Paraplex X-100 can be reinforced with neutral, finely divided pigments and vulcanized with organic peroxides to produce a truly synthetic elastometer with new properties. These physical properties are similar in many ways to the Buna N vulcanizate. The conditions necessary to produce the Paraplex X-100 vulcanizate and those set up during vulcanization, as well as the final properties, are quite different, however, from those of Buna N.

A new polymerization technique, different from that of existing materials, is used in the production of Paraplex X-100. Paraplex X-100 should not be considered just another new vulcanizable elastomer or rubber substitute. Although its vulcanizates are strong and have a snappy resilience like natural rubber, for which they would serve as an excellent substitute in many applications, the new material has several unique properties that are proving its usefulness in the field despite its relatively high cost.

The compounding of Paraplex X-100 is simpler than that of most elastomers. The polymer gum is devoid of nerve; hence, it requires no mastication or chemical plasticizer to produce a smooth sheet. The reinforcing agent and vulcanizing agent are the only additional materials necessary in the compounding operation and are added in that order. The uncured compounded stock exhibits excellent building tack, which is lacking in most synthetics. Solvent cements are prepared by the usual technique.

The curing cycle is rapid at common vulcanizing temperatures. Thin sheets have been cured in a matter of seconds at 30 lb. steam pressure, and the stocks are unusually resistant to overcure. Prior to curing, the stock goes through a period marked by unusually high flow. During the actual vulcanizing operation, the compound expands slightly. These two characteristics of high flow and expan-

* Manufactured by Resinous Products & Chemical Co.

sion during vulcanization make it possible to bring out the fine detail or intricate shape of a complicated mold.

Not only do molding and vulcanizing conditions differ from most synthetics, but the characteristics of the final vulcanizate are appreciably different. Tensile strength values in the range of 1500 to 1800 lb. per sq. in. are normal. Most stocks will show an elongation of 350 to 450 per cent. Permanent set, compression set, resilience and rebound are unusually good and of the order of natural rubber. Unusual resilience is one of the outstanding characteristics of Paraplex X-100. Its aging characteristics are good, according to both oxygen bomb and natural aging tests.

Paraplex X-100 vulcanizates are well suited to service at temperatures as high as 215°F. Other types not yet in commercial manufacture have proved adequate for temperatures as high as 300°F. Paraplex X-100 stocks are also well suited to low temperatures and, as shown by 20-min. exposures, will not embrittle at as low a temperature as −70°F. Stocks tend to embrittle, however, on extended exposures. After 24-hr. exposure periods, stocks will pass a bend-brittle test at temperatures as low as −40° to −45°F. The stocks will give service over a wide temperature range without the use of an extractable chemical plasticizer. Most oils and aliphatic hydrocarbons have little or no effect on Paraplex X-100 vulcanizates. Aromatic hydrocarbons, chlorinated solvents, ketones and esters cause swelling but remarkably little extraction. Thus all stocks except those compounded for unusually low temperature service show no appreciable extraction, since they contain no chemical plasticizer. Electrical properties at ordinary voltages have promise of value.

In most of its actual applications and in tests Paraplex X-100 has been employed without modification by other elastomers. Gaskets have been made of Paraplex X-100 that show no shrinkage or swell during operation in fluids that would attack or extract their elastomers.

Paraplex X-100 is still relatively new, and co-vulcanizates have only recently been considered. Many firms are now studying the possibility of modifying existing elastomers with Paraplex X-100 to improve specific properties. In one case, attempts are being made to improve an elastomer that is notably deficient in resilience. Para-

plex X-100 is being considered for improving flow properties in a Buna N molding composition and as a non-extractable, vulcanizable plasticizer. Blends of Paraplex X-100 and oil-resisting synthetics may be used for gaskets and closures requiring a good tight seal, wherein the non-extractable Paraplex X-100 will have the desired limited swell. Since certain organic substances required in the compounding of synthetics markedly retard the benzoyl peroxide cure of the Paraplex X-100, a sulfur-curing type that may prove to be a much better material for co-vulcanizing work is now being investigated.

It is anticipated that Paraplex X-100 will have many specialty uses; applications may be possible outside the field associated with elastomers. It is currently being produced only on a large pilot-plant scale. Larger commercial scale manufacture is expected soon.

MARBON S AND S-1.

Synthetic resins of the elastomer type have been developed by Marbon Corporation.

The use of 10 to 50 per cent of Marbon S or S-1 with GR—S (Buna S synthetic rubber), increases the modulus, tensile tear resistance, abrasion resistance and hardness of the GR—S compounds. The Marbon resins facilitate smooth tubing of "pure-gum compounds."

These resins are essentially hydrocarbons in composition and contain only minor quantities of other substances. The distinction between Marbon S and S-1 is that the S-1 is better electrically, but is slightly inferior in compatibility with the synthetic rubbers.

Following are properties reported for Marbon S and S-1:

	S	S-1
Specific gravity	1.05	1.05
Ash	0.4 to 0.6%	0.4 to 0.6%
Color	Light	Light
Softening point	50 to 60°C	45 to 60°C
Water absorption 28 days at room temperature	0.34%	0.40%
Heat stability	300°F or higher	300°F or higher
Dielectric constant (1 megacycle)	2.90	2.90
Power factor (1 megacycle)	0.001 to 0.002	0.0004 to 0.0009

Compatibility: compatible with natural and synthetic rubbers

Plasticizers: dibutyl sebacate, butyl stearate, dibutyl phthalate, tricresyl phosphate and diamyl naphthalene

PRODUCTION OF SYNTHETIC RUBBER

(Includes Production of Private Plants)

Long Tons

	1943 Actual	1944 Estimated	1945 Estimated
Buna S	184,781	712,376	700,000
Butyl	1,373	27,159	40,000
Neoprene	33,603	57,453	50,000
Buna N	14,487	20,049	12,000
Total	234,244	811,037	802,000

(Data from Rubber Director's Progress Report No. 6)

RAW MATERIALS NEEDED TO MAKE PRINCIPAL SYNTHETIC RUBBERS

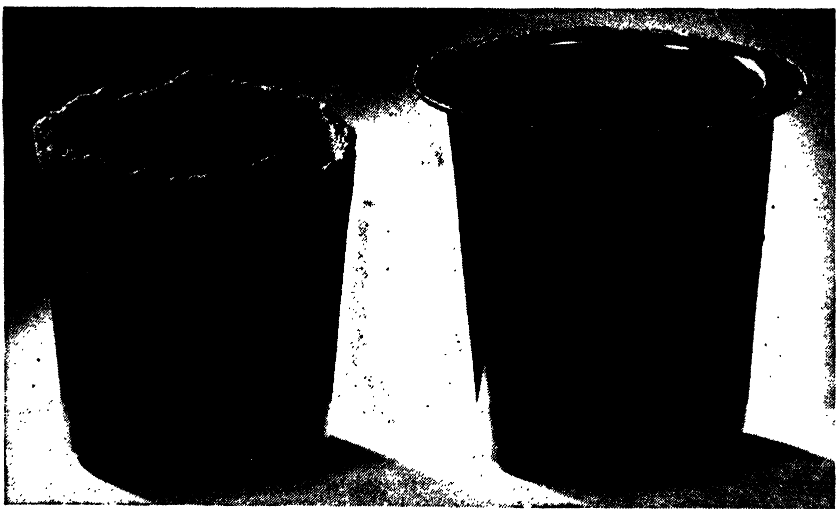
PETROLEUM . . . . Butane or →
Butylene →
NATURAL GAS . . . . Butane →
NATURAL GAS . . . . Ethyl Alcohol → BUTADIENE
POTATOES . . . . Ethyl Alcohol →
GRAINS . . . . Ethyl Alcohol →
SUGAR . . . . Ethyl Alcohol → BUNA S
MOLASSES . . . . Ethyl Alcohol →
COAL TAR . . . . Benzol →
PETROLEUM . . . . Benzol → STYRENE
PETROLEUM . . . . Ethylene
ETHYL ALCOHOL . . . . Ethylene
(SEE ABOVE) . . . . (See Above) — BUTADIENE →
PETROLEUM . . . . Ethylene
AIR . . . . NITROGEN ACRYLONITRILE BUNA N
LIMESTONE
COKE — ACETYLENE
AIR
CHLOROPRENE NEOPRENE
SALT
SULFURIC ACID
NATURAL GAS . . . . Isobutylene
PETROLEUM . . . . Isobutylene
BUTYL
(SEE ABOVE) . . . . Butadiene
or
Isoprene

CHAPTER X

New Processes

MOLDING WITH ELECTRONIC HEATING

AUTHORITIES in plastics are agreed that the most revolutionary new process in the industry is electronic or heatronic heating.



Courtesy Bakelite Corp.

FIG. 36. Test cups molded for general-purpose phenolic material. Total pressure, 800 lb. Left, standard molded, no filling. Right, electronic molded, 6 sec. close.

High-frequency or electronic heating is a method of converting electricity into a form that will cause the molecules in a substance to distort and rub together, thus setting up friction that results in internal heat.

High-frequency heating of nonconducting materials is similar to the more familiar induction heating of metals. The difference lies in the rapidity of reversal of current. For metals the rate is of the order of 3000 reversals per second while for plastics the reversal rate is of the order of millions per second. When polarity, or direction of the electrical field, is reversed, the molecules change shape with each reversal of polarity. Therefore a tremendous amount of heat is created by molecular friction when the electric field is reversed millions of times per second.

Induction heating of conducting materials such as metals has been used to a large extent in recent years, but it was only in the last two years (1943 and 1944) that the analogous process was developed for the heating of plastics preforms.

The history of the new development goes back to 1936 when the Thermal Engineering Corp. of Richmond, Va., a tobacco processor, was looking for a method of evaporating moisture from tobacco without removing it from the hogsheads in which it is stored and shipped. Obviously any method involving heat transfer would be slow and uncertain, and a way was sought to produce the heat directly in the tobacco, without transfer of heat from the exterior.

The solution was to make the tobacco the dielectric in a condenser subjected to a rapidly alternating potential and thus to take advantage of the usually undesired condenser losses. In order that these losses should be high enough for the desired heat release (that is, enough electricity converted into heat) an extremely high frequency of alternation was necessary, up into the millions of cycles and beyond the range of mechanical methods of generating alternating potentials. In order to meet this need, it was necessary to turn to the methods of radio transmission, and the resulting equipment involved a high-frequency electronic oscillatory system fundamentally similar to a radio transmitter, but more powerful.

Among the earlier applications of electrostatic heating were the killing of insect infestation in grains and cereals and setting of glues and resin cements in the manufacture of plywood.

More recently still, the process has been applied to the setting (curing) of resin glue layers in laminates and plywoods.

The war gave impetus to the latter development by creating a demand for quantity production of plywood airplanes and gliders. Radio engineers tackled the problem and increased the applications of the new process. Much of the foresight in the use of high-frequency heating and the development of suitable equipment should be credited to V. E. Meharg of the Bakelite Corporation.

High-frequency heating has been used to overcome what seemed an insurmountable problem in the production of airplane propellers from compressed wood. It is being used to expand the production of laminated and box spars, truss-type rib constructions, bomber floors, bomb-bay doors and other aircraft parts. It is being tested for use in making various molded-plywood forms such as wing elements and fuselages. It is being used experimentally for seasoning wood and drying aircraft quality plywood.

The new process will greatly widen the field of application of thermosetting materials such as the phenolics, ureas and melamines and will have far-reaching repercussions on the entire economy of plastics production.

Early in the development of cycle molding of thermosetting plastics, it became evident that one of the most severe limitations of the process was the length of time required to bring these materials to the molding temperature, particularly when molding thick sections. Despite a great many other advances in the art of molding, this limitation prevailed until recently and became somewhat of a bottleneck as other related operations were speeded up. Electronic molding affords a direct answer to this basic difficulty.

The rate of heating of a particular material in an electrostatic field is found to vary with the applied voltage, the frequency and the loss factor of the material. Materials with an extremely low loss factor, such as polystyrene, show low heating effects at frequencies commercially available. Most molding materials, however, have a relatively high loss factor and can readily be heated by electrostatic methods. In fact, all the present-day large-scale thermosetting resins and their commonly used fillers are satisfactory in this respect.

For a given heating rate, an increase in the operating frequency permits a decrease in the voltage gradient across the heating

condenser. Since the possibility of arcing across the heating plates varies with the voltage gradient, it is desirable to operate at the highest frequency available. The loss factor of several filled thermosetting molding materials in preformed state prior to molding is shown in Table I. Within the range covered, there is no great change in loss factor with frequency. There is thus a wide latitude for choice in frequency and voltage to give the desired heating rate, and the selection can be on the basis of availability, costs, operating characteristics and other governing factors.

When a preform of such a material is subjected to the high-frequency field, the heat is generated uniformly throughout the material, irrespective of its size, and the rate at which heat is developed is directly proportional to the power input. Thus the heat conductivity of molding materials, precluding size and weight as limiting factors, no longer has to be considered. It is theoretically possible to heat to molding temperature any quantity or weight of a thermosetting molding material.

Many methods of utilizing electronic heating are known, but one that has already proved highly useful applies particularly to compression and transfer molding. This consists in heating the preformed material to molding temperature in the electrostatic field set up outside the molding press, followed by quick transfer to the mold and rapid closing of the press to obtain flow prior to hardening. This transfer may be manual or automatic. Cycle controllers may be used to advantage. Other variations may be made to secure maximum speed of operation. For instance, the electrostatic heating field may be mounted over the mold and the heated material allowed to drop into the mold or else forced into it by the mold plungers. With a horizontal ram, the electrostatic heating plates may be mounted between the ram and the mold, and the ram may be used again to force the heated material into the mold.

Although preforms are used in the foregoing procedure, powder may also be heated if it is retained in a suitable container made of a superior insulating material of the ceramic type. However, it is easiest to obtain uniformity of heating if the material is of uniform shape, thickness and density, and this is readily achieved by use of

conventional preforms. Furthermore, this uniformity of heating is particularly important for thermosetting materials sensitive to precure or overcure.

Heating of the material in the mold itself is also possible with a special mold construction in which the top and bottom plungers are used as the heating plates, and the chase is made of an insulating member having special electrical and heat-resisting properties. Such a mold has been used and may prove acceptable for many special purposes, although it imposes limitations likely to restrict its general use.

Used under specified conditions, electronic molding has many outstanding advantages, some of the most important of which are the following:

Molding time has been decreased in all applications tried. This is true because heat transfer is an appreciable factor in virtually all fast cycle molding. Naturally, the advantage is greatest with thick molded sections. It will be noted that electronic molding gives a rate of cure that is independent of thickness. Production of thick sections, which have been costly, time consuming and often impossible, is of the greatest practical importance in expanding the applications of thermosetting plastics, as well as in eventually greatly lowering the cost of most molded parts.

Plasticity or flow properties are greatly enhanced by electronic molding. One important result is that molding can be made at lower pressure. This ensures a saving in press costs, by permitting either use of larger molds in available presses or use of smaller presses for the same molds. Many materials can be molded at from 25 to 30 per cent and others at from 40 to 50 per cent of the pressure previously used. Without reducing available pressures, harder flow materials may be molded.

Lower molding pressures lead not only to immediate savings in press costs but also to other important advantages. The wear on molds should be reduced and the problems in connection with insert shearing and displacement are greatly alleviated. Furthermore, many low-cost methods of producing molds that have been adopted in other related fields may now find use in the molding of plastics. Reduction in mold and other costs should enable the indus-

try to reach more users, especially those needing only small quantities of molded parts. Another market will be opened in the field of large moldings, not only those of thick cross section, but also those of large area. In lowering the molding pressure and reducing time of cure, the greatest obstacles to large parts are removed. Electronic equipment of such size has already been made available to permit immediate production of moldings up to 50 lb.

The advantages are obtained together with improved molded properties. Not only have strength and electrical values been retained, but time of cure has been greatly decreased. The reduction in cure time is achieved without sacrifice of thoroughness of cure as shown by acetone extractives. Not only do the conventional tensile and flexural strength values show improvement, but also the molded pieces are stronger because of less internal strains. This is especially noticeable in parts of thick sections, and those containing sections varying widely in thickness. This leads to better uniformity and more dependable strength values in molded parts. This may prove to be the most important of all advantages.

Proper heatronic molding requires uniform heating of the material prior to plastic flow and completion of flow prior to hardening, thus providing a uniformity in the molded piece heretofore not obtained. Improvement is also found in water resistance and electrical properties for many materials.

The many economies of electronic molding are obvious in savings in press, mold and labor costs. Some interesting data on the cost of electronic equipment and its effect on over-all cost are shown in Figs. 37 and 38. Experience has shown that the actual current cost per pound of material heated is around one tenth of a cent. The curves represent approximations on the basis of a few installations and will vary somewhat with different manufacturers.

Operating costs in equipment of this type are made up mainly of tube-replacement and power costs. Since there are no moving parts, other maintenance costs are negligible. The useful life of the equipment is long and is likely to be terminated by obsolescence rather than by wear. Depreciation can therefore be based only on some arbitrary figure such as that used for tax purposes.

In order to gain some idea of operating costs, a number of equip-

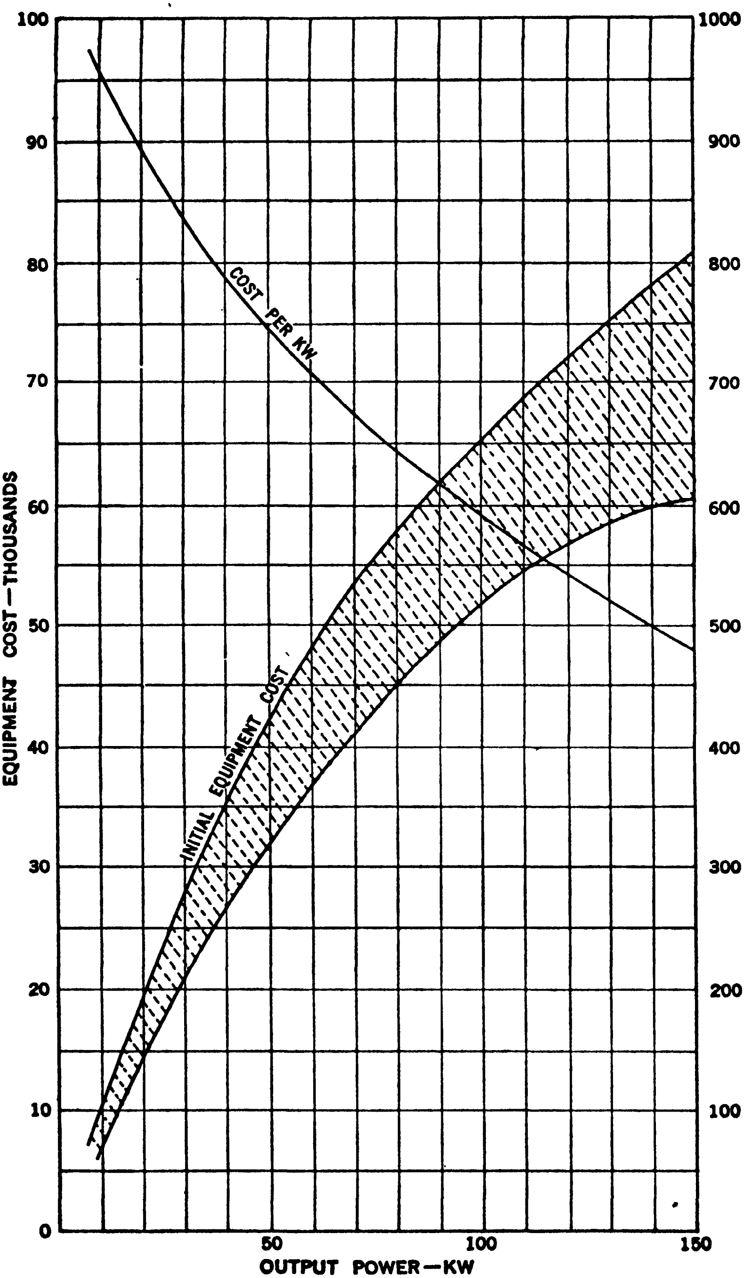


FIG. 37. Initial cost of radio-frequency equipment and cost per kilowatt.

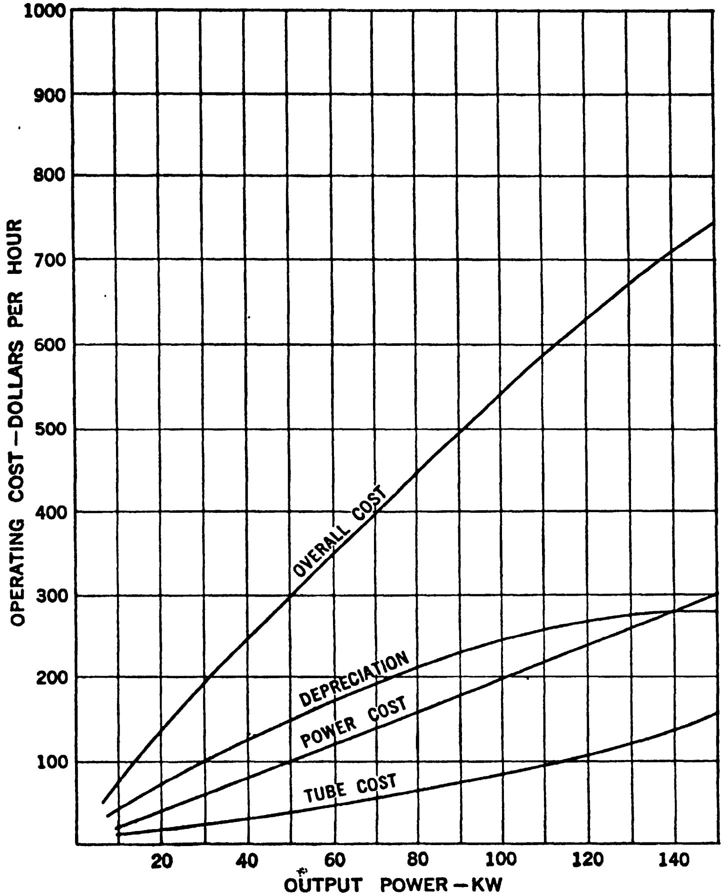


FIG. 38. Approximate tube cost, power cost, and over-all cost of radio-frequency equipment versus power delivered to load.

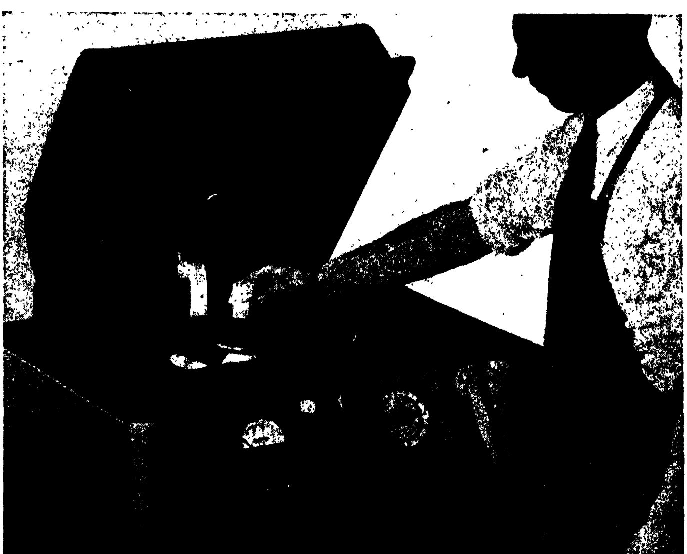
ment units of various powers were analyzed with the results shown. In this calculation, average tube life was assumed to be 5000 hr., a reasonable estimate of the life of present-day tubes in this service. Power was assumed to cost \$0.01 per kw.-hr. Depreciation was figured on the basis of 25,000 hr. of operating life (approximately 3 years at 24 hr. a day, or 9 years at 8 hr. a day). The over-all cost is simply the total of depreciation, tube and power costs.

Such costs, however, will probably be reduced in the future.

Simplification in design, improvements in tube construction and other factors that can be clearly foreseen will undoubtedly lead to lower initial as well as operating costs. Even on the basis of the costs as shown, however, it is apparent that many jobs can easily be justified from the cost standpoint.

SUMMARY OF ADVANTAGES OF ELECTRONIC MOLDING. 1. *Saving of Time.* Obviously a possible 50 per cent saving in the closing and curing portions of the mold cycle can be easily obtained. If press procedure and handling routine are specially arranged for rapid preheating by radio-frequency power, possibly a much greater time saving could be realized. This saving will manifest itself as increased production with existing press facilities or equivalent production with fewer presses.

2. *Improvement of Product.* Uniform heating throughout the preform not only results in a more thorough polymerization of the impregnating material, but should also tend to improve quality



Courtesy Radio Corp. of America.

FIG. 39. The preform is placed between terminals of a high frequency unit for heating. When desired temperature is indicated it is transferred quickly to mold cavity.

from the standpoint of residual stresses and consequent warpage or physical distortion. Also, less expensive molding compounds containing less resin, but yielding satisfactory finished pieces may be possible.

3. *More Intricate Parts.* An obvious advantage of preheating the molding material to a plastic state before insertion into the mold is the decreased stress on the mold parts. This is particularly true of intricate molds in which comparatively delicate inserts are placed. These are quite often broken off because of side pressures to which they are subjected by the semiplastic material flowing into the recesses of the mold.

4. *Thick Molded Sections.* Because of its ability to heat uniformly through the material, radio-frequency power is particularly well adapted to preheating thick sections or large preforms.

5. *Greater Economies in Production.* Many of these economies are apparent from the savings in press, mold and labor costs already possible. Further economies will no doubt result with improvements in equipment and processes that should be achieved in the future.

Recent Developments. The whole field of electronic heating is under study from a great many directions, and developments are occurring so rapidly that it is difficult to keep abreast of them, particularly during the war period when some of the newer applications have been restricted because of the need for military secrecy.

The Girdler Corporation of Louisville, Ky., which acquired the Thermal Engineering Corp. of Richmond, Va., one of the pioneers in the field of electronic heat bonding of plywood, reports the following recent developments.

During the war period it has placed a number of Thermex units in operation on critical jobs in various parts of the country. The following installations are indicative of the wide scope of application of electronic molding:

One of its standard No. 15-A Thermex units with preheater cabinet is in use heating preforms made of mascerated-rag phenolic material where the weight of the preform is 4½ to 5 lb. The thickness is 3 in., and the diameter is approximately 9 to 10 in.

A standard No. 8 unit with preheater cabinet in successful opera-

tion on a melamine asbestos head (the Scintilla magneto head, so much in demand for aircraft use) is at Donald Dew's plant, Diemolding Corporation, Canastota, N. Y.

The company reports that, although the equipment is capable of handling fairly large poundage, it can also be set up with complete automatic press and accessories and used on extremely small production parts such as are in common use in the automotive industry. The savings in time as well as in mold and press costs and the improvement in quality are so outstanding in one case that serious consideration is being given to revamping the entire plant.

Some interesting and unexpected results have been encountered. It was found, for example, that on many of the materials the shrink-

LOSS FACTOR OF MOLDING MATERIAL PREFORMS*

Megacycles	1	10	25	50
Phenolic wood flour filler	0.130	0.156	0.161	0.160
Phenolic asbestos filler.......	....	0.351	0.244	....
Urea cellulose filler..........	....	0.123	0.144	....

EFFECT OF METHOD OF HEATING ON FLOW CHARACTERISTICS OF MOLDING MATERIALS*

Type of Phenolic Molding Material	Type of Molding	Total Pressure, Lb	Mold Closing Sec
General purpose	Standard	17,000 (minimum)	25
	Electronic	17,000	6
	Standard	8,000	Not filled
	Electronic	8,000 (minimum)	6
Improved impact-resistant	Standard	14,000 (minimum)	35
	Electronic	14,000	4
	Standard	6,000	Not filled
	Electronic	6,000 (minimum)	4
High impact-resistant	Standard	30,000 (minimum)	32
	Electronic	30,000	11
	Standard	6,000	Not filled
	Electronic	6,000 (minimum)	12
High heat-resistant	Standard	16,000 (minimum)	25
	Electronic	16,000	13
	Standard	8,000	Not filled
	Electronic	8,000 (minimum)	13

* From a paper by V. E. Meharg.

age is reduced substantially, in one instance to 25 per cent of that which had previously occurred. The reduction was so marked that new molds were needed to use Thermex equipment satisfactorily.

The company reports that the greatest demand from the plastics industry seems to be for automatic equipment, where smaller plastics pieces are involved, and the operation is a highly repetitive one. To meet this demand, it has developed a special unit that operates at a frequency of around 25 to 30 megacycles and is simple in operation. Preforms are loaded on the drawer, by hand or by loading tray. The drawer is closed, automatically turning on the

PHYSICAL AND ELECTRICAL PROPERTIES OF HIGH IMPACT-RESISTANT PHENOLIC MATERIAL (BM-3510 BLACK) MOLDED BY STANDARD AND ELECTRONIC METHODS*

	Electronic Molded		Standard Molded	
	Cure Time at 320°F Min	Test Value	Cure Time at 320°F Min	Test Value
Tensile strength, psi				
Condition I	1¼	7,600	12	7,440
Condition II	1¼	7,840	12	7,050
Impact strength, Condition II, ft-lb/in. of notch	1¼	2.9	12	3.0
Flexural strength, Condition II, psi	¼	15,270	12	12,900
Compressive strength, Condition II, psi				
Parallel to molding pressure	1¼	23,900	12	34,400
Transverse to molding pressure	1¼	27,170	12	25,060
Insulation resistance (4-in. disk by ⅛ in. thick) megohms, Condition III	1½	5,000–	30	5,000
Condition II	1½	6.3	30	6.6
Dielectric strength (4-in. disk by ⅛ in. thick), Condition II, v/mil	1	S/T 144 S/S 72	12	S/T 157 S/S 92
Dielectric strength (4-in. disk by ½ in. thick), kilovolts				
Condition III	1½	20–	30	20–
Condition II	1½	6.8	30	5

From a paper by V. E. Meharg.

* Condition I — As molded. Condition II — After 48 hr immersion in water at 50°C. Condition III — After 96 hr at 70% relative humidity at room temperature.

S/T — Short-time test. S/S — Step-by-step test.

high-frequency power and the timer. At the end of the prescribed time, which may be anything from 5 to 10 sec. up to 2 min., the red indicating light goes out, the operator removes the tray and unloads the preforms into the mold cavities. There are no adjustments for the operator to make, and it is only necessary that he load, close and unload the tray. It is not even necessary to push a button, for the closing of the tray accomplishes this.

JET MOLDING

The possibility of applying injection molding to thermosetting materials has long intrigued research workers in the plastics industry. One of the decisive advantages of the thermoplastics has been their ready adaptability in injection molding with its economies of large-scale production, and this has more than offset the lower material costs of some of the thermosetting materials.

A method of molding thermosetting plastics by injection has been developed within the past few years and is known as jet molding. It is based on the patents of Clement D. Shaw, U. S. Patents 2,296,295 and 2,296,296, which are held in trust by W. B. Hoey and Everett D. McCurdy. Plastics Processes, Inc., 2500 Terminal Tower, Cleveland, Ohio, is the licensing agent for these patents.

The process has been used during the war by a number of concerns for the high-speed production of thermosetting moldings. Its potential use, however, is not confined to the heat-setting plastics. It can also be used for molding thermoplastic materials, including natural and synthetic rubbers. The method seems to offer a practical solution for the handling of some of the newer thermoplastics which are highly heat sensitive and break down in the heating cylinders of the conventional injection machines.

The basic principle of jet molding lies in the fact that all heat required for polymerization is applied to the material prior to injection. The process can therefore be used on standard injection molding machines equipped with special conversion units. The conversion units consist essentially of a special heater with temperature indicator and control, and a feed cylinder and plunger. The nozzle of the unit is continuously watercooled. During the same instant

that pressure is first applied to the plunger, extreme heat is generated briefly in the nozzle. Thoroughly plasticized by this heat, the thermosetting material flows freely, in a thin, highly fluid stream, into the heated mold where it sets quickly.

Because the nozzle is cooled immediately after being flash-heated, and the injection stroke is completed, the material in the nozzle does not set up, but remains highly plasticized, awaiting the next heat wave and injection. Thus a constant supply of free-flowing material is maintained for fast, uninterrupted production.

Owing apparently to the high fluidity of the molding material at the instant of injection, jet-molded parts are extremely dense, free from porosity and seemingly toughened by the high temperature employed. Intricate parts, with numerous delicate inserts, thin sections and close tolerances, are molded easily and rapidly with minimum rejects. Moreover, tests of molded parts turned out by the jet process indicate properties superior to those of standard compression-molded pieces. Each section, thick or thin, exhibits full-rated strength. Uniform quality, as well as great speed, is an outstanding production feature.

All types of molding compounds, characterized by various degrees of bulk factor and plasticity, are fed into the machine through proper hopper mechanism and are molded with apparent gains in quality, ease, speed and over-all economy. Standard A.S.T.M. mechanical, electrical, thermal and chemical tests show improved properties.

The primary reason for better results is that the method produces optimum plastic softness in the material, enabling it to flow properly under minimum pressure, filling the mold in minimum time and without porosity. Such is the basic principle of efficiently molding thermosetting plastic compounds: coordination of temperature, pressure and time to obtain optimum plasticity in the initial softening period, which may vary from mere mobility to relatively high fluidity.

Molding compounds vary in their thermal conductivity, largely because of the effect of fillers on the conditions of flow. Most thermosetting resins are inherently poor thermal conductors. The molder endeavoring to produce sound and uniform molded pieces offering

the maximum in desirable properties must endeavor to determine and apply a combination of heat and pressure best calculated to assure these properties in a molded piece of given design, and yet he must keep the time element within the limits of molding cost.

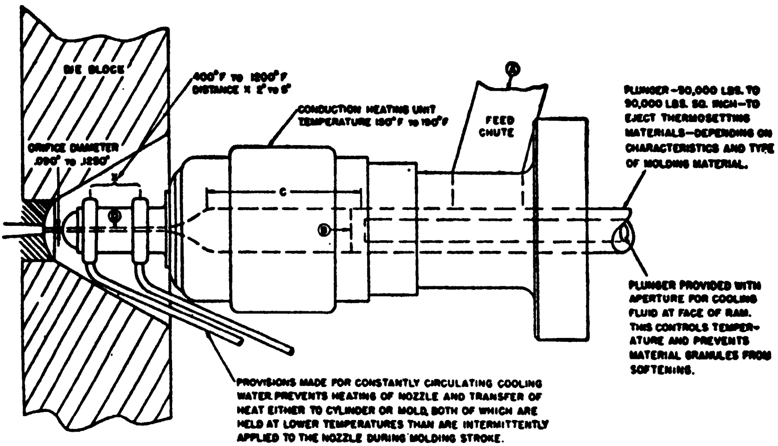
Ordinarily a molding charge is heated, pressure being applied simultaneously to conform the softened compound to the shape of the mold cavity, where it is held under pressure until the heat-setting, or polymerization, period is completed. In this operation, free flow involving optimum fluidity is obviously of the greatest importance.

Present compression-molding technique consists primarily in conduction, through the walls of the steel mold, of heat derived from steam, electricity or gas. It has the disadvantage of causing the heat penetration into the molding charge of either powder or compressed preform to heat first the outer surface and then gradually penetrate the center of the charge. Thus, the degree of the heating, and with it the curing or setting of the preform, progresses in varying stages from a degree of casehardening or preset at the outer surface, to a soft spongy condition at the core or center of the preform. This naturally defeats the type of heating of the charge required for the best molding. Trapped gases and varying cure throughout the mass necessitate higher pressures to form the plastic.

Figure 40 shows the jet-molding nozzle principle of the conversion unit adaptable to standard fully automatic injection-molding machines. Jet molding of thermosetting materials eliminates the mass heating of a given molded charge, as in compression molding. The charge by the jet-molding principle, as applied with a standard thermoplastic injection-molding machine, is placed in a hopper and is gravity-fed through a chute into a feed cylinder sleeve (*A*). Standard powder materials, grains, chips, flakes or other convenient forms may be fed into the cylinder.

The material is moved forward by a plunger (*B*), provided with an internal aperture to ensure cooling of the plunger face, which prevents the granules from softening at this point and creeping around and building up on the sides of the plunger.

The material goes through an effective heating zone where a controlled temperature of 150° to 190°F. exists (*C*). Continued



Courtesy Bakelite Corp.

FIG. 40. Jet molding nozzle principle.

pressure exerted by the ram causes the heated charge to flow. No detrimental reaction takes place in the cylinder because the temperature maintained at that point is too low to permit any heat-softening and subsequent heat-hardening.

As the ram continues its forward movement against the softening charge at the end of the cylinder, the charge is forced into the ejection nozzle (*D*), which is heated while ejection is in progress to a temperature anywhere between 400° and 1200°F., according to need. The temperature is controlled carefully in accordance with requirements, depending upon the composition of the plastic being worked, the amount and nature of the filler it contains, if any, the size and complexity of the mold and other factors.

The charge is ejected in a fine stream. It receives heat in the nozzle just before and during its ejection, a momentary period. Its velocity is such that the charge does not, however, attain a temperature equal to that of the nozzle at the instant of ejection. Possibly circulating cooling water, flowing through the heating tips, prevents transfer of heat from the nozzle to the cylinder or the mold, both of which are held at temperatures lower than those intimately applied to the nozzle. This cooling also enables the material to be solidified to the nozzle channel, if and when desired.

Such solidification seems to be without polymerization; whatever the explanation, in practice the material can again be made to flow under heat and pressure after being held so solidified in the nozzle for several hours.

The temperatures maintained in the mold are also controlled in consonance with factors similar to those which determine the temperature to be used in the nozzle. Normally, the mold temperature will be 300° to 325°F., although for certain types of work, temperatures of 400°F. or more may be employed. The temperature is not critical, for it has been found practical with jet molding to run the mold somewhat hotter than necessary without injuring the material.

The time of injection, or plunger speed in inches per minute, is determined by the factors that govern the nozzle temperature, including quantity of material ejected in each shot, the characteristics of the material, flow distance, etc. Definite electric controls for speed of the ejecting stroke and for heating the nozzle are coordinated as to both heating elements and plunger travel.

The heating elements are of the induction type, such as are used in resistance spot-welding apparatus. With this type of heating, instantaneous and high temperatures can be generated on the nozzle so that the nozzle passages will be heated to a temperature that will liquefy the molding material as it is ejected through the passage in a thin, fast-moving stream. The temperature to which the material is subjected is much higher than it could withstand for any substantial period, but, since it undergoes this intense heat for only a fraction of a second, no harmful effects occur.

In molding heat-setting materials, the various types of phenolic compounds can be worked to good advantage, including the fabric- and paper-filled materials of the stronger impact types, also the many colored, translucent, and pastel ureas and melamines. Thus, by adaptation through this process, the injection machines become a universal molding combination, permitting high-speed production by continuous injection molding.

Advantages of Jet Molding. Three outstanding advantages of jet molding of thermosetting materials are:

1. It is faster than compression molding. The speed of curing thermosetting materials is only a fraction of the flowing and curing

periods usually required in conventional compression molding. Injection is fast and continuous. There are no bottlenecks arising from cylinder cleaning or freezing of fluid materials.

2. The molded parts are more likely to have excellent and uniform molding characteristics, whether of thick or thin section. The surface finish is usually good, with no surface sticking to stagnant areas, such as commonly occurs in some types of compression molding. Because of the uniformly good surface finish, the molded pieces often do not require buffing.

3. Dies required are smaller and more economical. Delicate inserts now being incorporated in intricate molded parts are undisturbed by jet-molding processes; also simplified mold construction is possible.

However, it is too early to prophesy just how important a place in the industry jet molding will occupy, for the economics have still to be worked out, and other processes are being developed.

LOW-PRESSURE MOLDING OF LAMINATES

The use of low pressures in the synthetic-resin bonding of laminates, particularly wood veneer, was developed in World War I in connection with the manufacture of curved sections of plywood, but its real usefulness was not proved until the war was nearly over. In the intervening years, several methods of fabrication involving variations in the basic rubber-bag, or diaphragm, process have been developed.

World War II has again brought this process to the fore. The scarcity of basic raw materials and the necessity of finding replacements for existing metal parts have created a considerable demand for low-pressure laminating. Fabric- and paper-base laminates, however, have largely replaced wood, because they are superior in formability and have more uniform strength characteristics.

The three variables in all plastics laminating and molding processes are time, temperature and pressure. It has long been the goal of the research engineer to reduce each of these as much as possible, not only to effect economies but also to broaden the field of application for plastics.

This has already been accomplished to a remarkable degree for molded plastics through such processes as transfer, jet and electronic molding. After several years of intensive research, it is now also possible to mold laminated products at low pressures and at reduced temperatures with a consequent saving in molding time. This has been due in large part to the development of special resins or modified resins and the adaptation of molding techniques from other fields.

The time interval for producing laminated products may now be a few seconds or many minutes. The pressure applied may be simple contact pressure of ¼ lb. per sq. in. effected by a small weight, or it may be the transmitted force of high-pressure hydraulic pumps. The temperature may vary from 70° to 500°F.

Low-pressure molding is a method of distributing a relatively uniform low pressure over a prearranged, resin-bearing, fibrous assembly of cellulose, glass or asbestos, with or without the application of heat from some external source to form a cohered laminated structure possessing definite physical properties. Thus, the low-pressure molding of laminates supplements high-pressure molding and consequently enlarges the field of application for laminated plastics in general.

Some of the factors that make low-pressure laminating practical are the limited availability of pressing equipment and molds, the time and capital allotted to produce finished molded products, the necessity for producing a certain number of parts in a given period and uncertainties in some industries regarding standardization of designs and dimensions. The types of molds and pressure-actuating systems for the processes are numerous. The following have already been used:

1. *Hot Press Type.* Cast-aluminum male or female mold sections with a rubber bag; hydraulic pressure; also cast-metal force and metal chase with a rubber bag (flat bag).
2. *Hot Press Modification.* Cast or welded female molds, steam jacketed; rubber bag inserted in cavity; air or hydraulic inflation.
3. Combinations of cement and wood, plaster of Paris and wood,

TABLE I. GENERAL TYPES OF RESINS USED IN LOW-PRESSURE MOLDING

Resin Class	Resin Type	Hardening Temperature*	Molding Time	Molding Pressure
Phenol-formaldehyde	Cold-hardening	70–140°F	30 min–12 hr	Contact–75
	Warm-hardening	140–220°F	15 min–2 hr	Contact–250
	Hot-hardening	280–360°F	5 min–1 hr	Contact–250
Amine:				
Urea	Cold-hardening	70–140°F	10 min–4 hr	Contact–75
Thiourea	Warm-hardening	140–220°F	5 min–15 min	Contact–200
Melamine formaldehyde	Hot-hardening	260–300°F	5 min–1 hr	150–250
Thermosetting ester resins	Warm- or hot-hardening	140–325°F	5 min–2 hr	Contact (½–2)

* The longer hardening periods generally refer to the rubber bag-autoclave process.

plaster of Paris and metal, metal-faced wood, cast-metal chase and cast-metal force plugs.

4. *Autoclave Method.* Wood, cement, metal forms with a rubber bag; reduced pressure in bag and hot air, air and steam, steam or hot water in the autoclave.
5. *Rubber Blanket Process.* Metal mold with rubber blanket on one side, assembled between platens of hydraulic press.

Three general types of resins now used for specific applications are shown in Table I.

Many of the cold- and heat-hardening resins were developed for the plywood industry. Variations in the formulations of the "hardeners" produce different hardening and plasticity characteristics at various temperatures and pressures.

The thermosetting ester types, some of which had only theoretical importance a few years ago, have found a useful place in low-pressure molding applications. These types of liquid resins, because of the absence of solvents, may be processed without drying the coated fabric. The assembly of wet sheets is placed in the mold, or a continuous web of the coated material may be wound on forms or mandrels. It may be necessary to add thickening agents to the liquid resins to prevent migration or flow of the fluid resin during the initial molding or baking cycles. Dimensional stability of thermosetting ester laminates, like that of the phenolics, is good.

In general, the phenolic resins produce tougher and more dimensionally stable structures than the urea-type resin syrups, although it is possible to improve the toughness of urea laminates by a variation in the distribution of the resin within or on the surface of the fibrous sheet. It is sometimes necessary to increase greatly the amount of resin applied to the fabric to produce a "mat" which is embedded in a mass of resin. The resin content may then be as high as 80 per cent.

The strength and toughness of molded laminates depend upon the resin and the filler. Excess acidity of the resin should therefore be avoided because of its tendency to embrittle cellulose fibers. Some thermosetting resins, when used to produce glass cloth lami-

nates, give excellent strength characteristics, while the same resins may cause embrittlement of cloth- or paper-base laminates.

The presence of sizing in fabrics also has its effects on the strength of laminates. When a desized fabric was used with a phenol-formaldehyde resin, the tensile strength of the laminate, as compared with a laminate made with a sized fabric, increased 25 per cent, but the impact strength was reduced 30 per cent. It is possible to increase the toughness of sizing fabrics with thermoplastic resins and bonding with thermosetting resins.

The bulk factor or density of the filler influences to some extent the minimum pressure that may be used. In general, increased bulk means higher resin content to effect flow at any given low-molding pressure. Low-resin-content, high-density papers and tightly woven fabrics mold at lower temperatures than the waterleaf type of papers or open-weave fabrics, although materials having a low density are likely to spread or fill out the contours of the mold better. This is particularly true in molding complicated shapes.

When the highest tensile strengths are required in a particular design, movement of the fibers is not permissible. In such instances, prepared shapes of high tensile paper, glass cloth, etc., are assembled in the mold. Where high-tensile strength is not a prime requisite, but speed in assembling the materials and in charging the mold is important, creped resin-filled paper, pulp forms, resin-fiber board preforms or a loosely woven resin-treated fabric may be used. This also results in a minimum of material waste.

Directional strength may be imparted by introducing strips of high-tensile paper, cotton threads or cords having very little twist, steel wire, glass fiber continuous-filament thread or yarn, metal inserts, strips of wood, sheets of oriented cotton fibers, battings of oriented threads and fibers, perforated metal or woven wire.

Resistance to abrasion and water, as well as improved finish, may be given to plywood panels by a surface layer of resin-treated paper or fabric which may be either molded directly to the plywood core or molded separately and then glued by the hot- or cold-press method to the wood. Normal wood-bonding pressures are effective in producing such a composite structure.

TABLE II. MECHANICAL PROPERTIES OF CLOTH, PAPER AND FIBER GLASS LAMINATES

Type of Filler	8.6-oz Duck 78 × 28	8-oz Duck	Special Sulfite	Special Sulfite	Fiber Glass (4)
Type resin	Phenol-formaldehyde	Phenol-formaldehyde	Phenol-formaldehyde	Phenol-formaldehyde	Phenol-formaldehyde
Molding time, ⅛-in. panels, min	8	8	8	8	8
Molding pressure, psi	100	200	100	200	250
Molding temperature, °F	310	310	310	310	310
Resin content, %	52	52	37	37	50
Volatile matter content, %	7.0	7.0	5.5	5.5	5.0
Specific gravity	1.31	1.37	1.37	1.40	1.65
24-hr water absorption (1 × 3 × ⅛ in.) test piece	2.8	2.0	2.5	2.5	0.9
Tensile strength, psi	11,500	12,200	36,000 (1) 18,000 (1)	34,000 (2) 17,000 (2)	45,000 (3)
Flexural strength, psi	21,900	22,200	35,000 20,000	35,000 20,000	45,000
Modulus of elasticity	0.88×10^6	0.93×10^6	3.0×10^6 1.5×10^6	3.0×10^6 1.5×10^6	2.0×10^6
Impact strength, Izod, ft-lb/in. of notch	A 3.8	4.0	0.8 0.6	0.8 0.6	16
	B		5.0 2.0	5.0 2.0	16
Compressive strength perpendicular to molding pressure	15,000	18,000	18,000	18,000	
Per cent elongation (tensile) 1 in. at fracture, %	4.88	4.82	2.5	2.5	

NOTES

(1) Parallel laminated machine and cross machine directions.
(2) Parallel laminated machine and cross machine directions.
(3) Cross laminated — very thin cotton fabric bonding films between glass fabric.
(4) Continuous filament warp, thin cotton thread welt.
A. Edgewise.
B. Flatwise.

Some of the products made by low-pressure molding are the following:

Molded wing tips	Funnels
Pilot seats	Terminal boxes
Flooring	Photographic equipment
Ailerons	Data cases
Wing tabs	Fairings
Tail cones	Doors
Ammunition chutes	Air ducts
Wing and fuselage sections	Instrument cases
Air deflectors	Jettison gas tanks for aircraft
Inspection covers	Small boats for the Navy

Some of the above applications suggest important peacetime uses. Thus, a small Navy boat is not far removed from a portable dinghy or a lightweight bathtub. Aircraft air ducts suggest noncorrosive air-conditioning and ventilating ducts. Pilot seats point to molded plow seats and school-room seats. Since size of moldings can be much larger, refrigerator cabinets, kitchen cabinets and lockers may be made by low-pressure laminating molding.

MASS PRODUCTION OF PLYWOOD

Many advancements have been made step by step in the manufacturing technique through the entire plywood operation, but as yet a continuous flow of production that might be compared with the manufacture of paper or metal has not been achieved.

A modern Douglas-fir plywood plant today employs straight-line production methods somewhat like those used in the manufacture of automobiles. The units are long lengths in standard sizes up to 60 in. in width and 120 in. in length, and in various standard thicknesses from $\frac{3}{16}$ to $1\frac{3}{16}$ in. These are in single-sheet form. Much larger panels can of course be produced by scarf-joining.

For the best grades of plywood straight-sliced veneers are edge-glued to form sheets which are then superimposed with glue interlayers and then bonded with heat and pressure. For the commoner types of plywood, veneers are peeled from round logs or bolts.

These latter are placed in giant lathes and rotated against long knives, which peel the wood in continuous, thin sheets. Most of these lathes can handle bolts up to 135 in. in length and a diameter of 110 in. They have variable speeds with a maximum of approximately 70 r.p.m. As the veneer is cut from the bolt, it travels into long conveyors known as transfers. These are approximately 250 ft. long and decked six high. The transfer is power driven and is synchronized with the speed of the lathe as it is cutting.

This operation is followed by clipping, drying and grading. The modern veneer drier is 14 ft. 6 in. wide and has five lines. It is approximately 90 ft. long, including the cooling section at the back of the drier. It requires about 7 min. to dry one-tenth heart veneer down to 2 per cent moisture content.

The huge presses used may have 12 to 16 dividing plates and are equipped with automatic loaders and hydraulic lifts. The glue is spread on the core or cross band of a panel. Three principal types of glue are used, moisture-resistant with a soybean base, water-resistant with a casein base, and waterproof with a phenolic resin.

After the panels are "laid up," the assembled veneer is manually fed into an automatic loader. This loader not only charges the press, but discharges in the same operation the previous load in the press. The pressing cycle will vary from 3½ to 8 min., depending upon the thickness of the panels being prepared and the type of glue used.

After the panels come out of the press, they are moved on trucks and passed through a series of saws, which rip them to width and cut to exact length semiautomatically.

PROGRESS IN FABRICATING EQUIPMENT

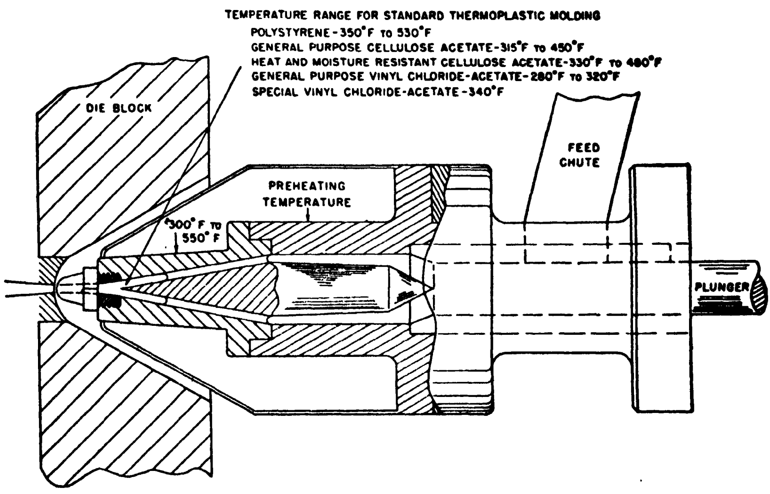
Of the many changes in fabricating equipment for plastics during recent years the following seem most important:

1. Electronic heating in combination with automatic, self-contained compression presses.
2. Greater strength, speed, and capacity of injection presses.
3. Jet molding for injection presses, thus introducing thermosetting materials to injection machines.
4. Higher temperatures and pressures in press design as result of new materials handled.

5. Application of transfer molding to injection presses.
6. Greater precision and control in extrusion machines.

The injection machine improved in many respects. Of these, capacity was most important. The 2-oz machine was practically removed from production. The 4-oz. machine became semiobsolete. The 6-, 8- and 10-oz. presses were the most popular.

Larger capacities, particularly 16 and 22 oz., received considerable publicity. A number of machines in these large sizes were manufactured but the demand soon became saturated. In the mid-West, where emphasis is on large single-piece moldings, these machines find most use. Preliminary investigation in the Eastern states points to the possibility that large machines are not the an-



Courtesy Bakelite Corp.

FIG. 41. Injection molding nozzle principle.

swer for increasing production of small moldings. Large machines, however, allow large-surfaced moldings to be made of thermoplastic powder.

Improvements in the design of the heating chamber increased capacity, but did not allow heavier shots to be operated on a faster cycle. Small capacity machines did achieve faster cycles, but with

heavier shots, a longer setting or cooling period was required thereby causing slower cycles.

Zone heating control became universal practice. Previous cumbersome methods gave way to accurate pyrometer control at several points on the heater.

The design of a heating cylinder for Saran was an important problem in 1941. The internal "hot zones" had to be made of a material that would not cause decomposition of the Saran. Chrome plating was not sufficiently foolproof and a material called Hastelloy was adopted.

The jet-molding heater was another problem.

Nylon required a special nozzle on the heater. This contained a screen pack to prevent the nylon from seeping and to act as a homogenizer and mixer for the plasticized nylon particles.

Changes in the heating chamber were accompanied by other improvements, the chief results being: large size thermoplastic molding and increased capacity of the standard sized machines.

The compression molding industry received a great impetus from electronic heating which was introduced shortly after the announcement of jet molding threatened the compression press. Electronic heating seemed to come as a godsend but both processes quickly found their relative levels.

Electronic heating greatly improved the speed of cycle and quality of the compression-molded article. These advantages increase with heavier castings and here is where electronics plays its most useful role.

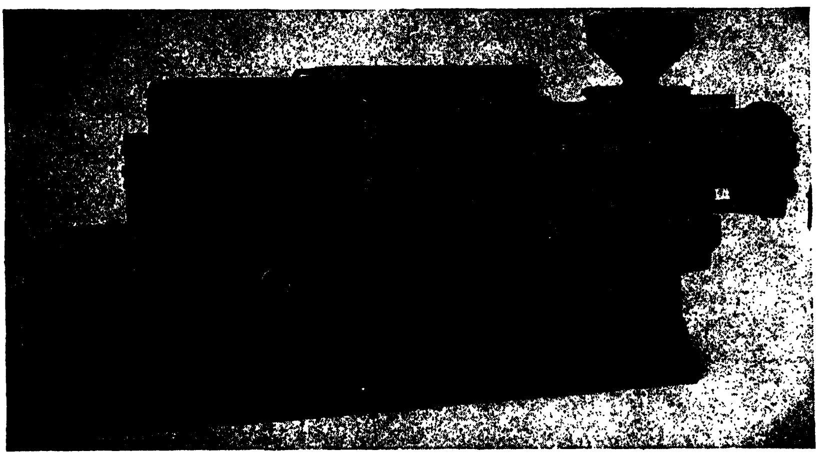
Other less spectacular changes were made. A growing trend to self-contained units and to automatic presses appeared. Pilling machines for improved material handling increased in use. Speedier presses were built to give full utilization of electronic heating.

Jet molding started a trend in the injection-molding industry by introducing thermosetting materials to the injection press. In ordinary compression presses excess material is removed after each cycle and is discarded. Jet molding provides a means of plasticizing only the correct amount of material for each shot. Thus there is no excess to be removed and the cycles continue in succession.

The impetus provided by jet molding brought another means of

molding thermosetting material on an injection press. This was to change the heating cylinder for a chamber which actually converted the machine into a "cold-chamber" die-casting machine. Pills of thermosetting powder are introduced into the chamber and injected into the die in the same manner as with aluminum or brass. The pills may be preheated or may be heated in the chamber. This process, still in the development stage, provides good production speed with less labor, and a saving in waste material.

In straight injection molding there were a few changes in technique, of which one was a lengthening of the cycle to give an



Courtesy Bakelite Corp.

FIG. 42. A modern automatic injection molding machine is a compact, rugged unit.

improved product. In earlier years, the speed of the injection machine was its outstanding feature. Cycles of 10 and 12 sec. were common. These cycles were and still are satisfactory for producing small, thin-sectioned articles from an easy-flowing material. As the type of molding progressed to include heavier sections and complicated articles, the cycle necessarily slowed down. Cycles of 30 to 60 sec. are now frequent.

Perhaps the most significant change of all in both injection and compression presses resulted from the change in materials due to

wartime restrictions. Because of lack of uniformity of molding powder, the molder cannot always count on his cycles and heats in advance of actually testing them. Minor changes in ingredients alter cycle and heat considerably and new designs have taken this into account.

EXTRUDING POLYSTYRENE

Polystyrene, upon heating, remains relatively hard and unchanged up to the transition point, then passes to a rubbery state having a strong elastic memory and as the temperature is increased becomes more and more like thick molasses. Stretching during the rubbery stage modifies the strength characteristics and extruding operations therefore must be carefully controlled. Strength is increased when the tensile forces are parallel to the direction of flow and reduced when they are in the direction at right angles to it. Polystyrene sheet stock that has been stretched to perhaps four times its original length becomes weak and brittle when bent crosswise. Strips or bars which, because of their shape, cannot be bent sidewise can be raised from 7000 lb. per sq. in. to 15,000 lb. per sq. in. A round rod when bent back and forth will split lengthwise. Sheets of a few mils in thickness can, by orientation, be made to have a tensile strength of perhaps 20,000 lb. per sq. in., and can be stretched cold up to 50 per cent. These sheets are weak crosswise, however, and thus far have been produced only in the laboratory.

Sheets in the finished thickness of 0.020 in. or less are practicable and are sold under the trade mark of Polyflex by Plax Corp. Sheets up to 0.010 in. can be bent double, punched, cut, sheared and otherwise handled without exhibiting the brittleness commonly associated with polystyrene.

Tubes made from laminated Polyflex are remarkably strong to bending or collapsing forces but are sometimes not entirely satisfactory for pipe and the like since the forces acting on the threads tend to tear them off.

Shapes that are extruded fast at temperatures less than 300°F., with powerful extruders, and are rapidly cooled exhibit pronounced orientation characteristics. Polystyrene tubing, for instance, so extruded and rapidly drawn away from the die will be strong

against bending but is prone to crack axially if subjected to impacts. Strength characteristics in all directions will be more even the hotter the piece is when extruded and the less its shape is changed.

Its prospective use often determines how an extruded piece must be made. The material should have little elastic memory when used for rods that are heated and bent in subsequent forming operations, for tubing that has been stretched from a larger die to a smaller diameter or for flat sheets heated for bending.

Polystyrene must be more uniformly heated for extrusion than most other plastics. If this is not done, the extruded piece tends to readjust itself into the shape of the original grains, and the surface becomes lumpy and rough. Attempts to avoid this trouble by higher temperatures and an extensive system of breaker plates are only partly successful owing to the poor heat conductivity of the material.

Extruders currently used on sheet machines are equipped with an auxiliary cold section that permits all the extruder barrel to be heated to the same temperature. This is followed by a breaker chamber, also heated to the same temperature. The die section may be heated by the same system of piping.

Flash heating of the die lips for uniformity of temperature on tubing and rod has thus far proved impracticable on wide, thin sheets. On 3½-in. extruders outputs usually are between 20 and 70 lb. per hr.

Polystyrene is neutral toward iron, and no special alloys are necessary for chemical purposes, but both the screw lands and the barrel must be hard to withstand the heavy back pressures which, in polystyrene, run from a minimum of about 700 lb. per sq. in. to nearly 3000 lb. per sq. in.

Most polystyrene tends to develop bubbles when extruded into the atmosphere. These bubbles are a vapor-pressure phenomenon and can be suppressed by applying outside hydrostatic pressure to the plastic.

Polystyrene has a low coefficient of thermal diffusivity and a relatively large modulus of elasticity. It is, therefore, difficult to cool round rods larger than ¼ in. in diameter from extrusion temperature to room temperature without inducing an interior vacuum, and it follows that bubbling will result. A die developed

by Plax Corp. maintains the plastic at or near its softening point for a long period of time and also at the same time holds the shape of the extruded piece and permits it to travel along through the die until the temperature at the center drops so low that bubbling will not develop.

Polystyrene is best handled at temperatures that give a frosted or matte finish. If polished rods are wanted they are made oversize to permit finishing to exact size.

After extrusion, the rod is carefully supported to permit equal cooling and to prevent surface marking. An automatic knife cuts the rod to any desired length.

Fine filaments are made by extruding through a multiple die.

Tubing is extruded conventionally. Drafts, unless carefully controlled, must be avoided; there must be no unevenness in the speed of the take-off conveyor or other parts of the mechanism. Air pressures used in blowing or cooling must be not only oil-free and water-free, but carefully controlled as to pressure and temperature. The molding powder must have a low volatile content, yet it must have reasonably free flow. Its grain size must be uniform also, making it necessary at times to screen out the fines. Given all these specifications, and a good degree of skill on the part of the operator, tubing of commercially acceptable quality can be extruded.

Toughness can be increased by blowing the tube to a larger diameter while, at the same time, drawing it out, thus giving it two-directional strength.

The equipment used to extrude unoriented polystyrene sheet consists of an auxiliary loader kept cool by water; an extruder, the entire cylinder of which is heated; a large homogenizer, also completely heated; and a 16-in.-wide nozzle. All may be heated by the same system of circulating oil. The sheet is drawn through a series of flattening rolls by a puller. Sheets up to 0.090 in. thick, 16 in. wide and of continuous length are made. After going through the puller, the sheets are hand-cut to length.

The surface produced is a fine matte. The higher the temperature, the more glossy the sheet becomes, but the formation of fine bubbles at high temperatures precludes the possibility of producing a sheet having a high degree of gloss and transparency. Flashing

the lips to produce a gloss has not been practicable owing to the large masses of metal involved and the difficulty of keeping a constant heating effect over such a great width. Irregular heating produces regions of off-gage thickness and warpage.

Satisfactory sheet can be made only from certain special grades of molding powder. Press polishing has been resorted to when high gloss and transparency are required.

The general arrangement of the loader, extruder, homogenizer and nozzle is similar to that used for extruding unorientated sheet, except that the nozzle is narrower and designed to extrude a thicker sheet. From the nozzle until the sheet is cool and stiff, the extruded sheet must be totally enclosed in a carefully zoned oven so that the temperature of the plastic undergoing stretching is accurately con-

Courtesy Plax Corp.

FIG. 43. A major development has been the successful extrusion of polystyrene in wide sheets. This shows such a process.

trolled. The forces involved in stretching the sheet are large. Since the sheet is stretched both laterally and longitudinally "on the fly," the movements must be accurately coordinated. During the stretching process, the area of the sheet may be increased from 8 to 12 times with a corresponding decrease in thickness. The stretching

must be done in the rubbery temperature range, a short distance above its softening point. In this range, polystyrene will tear easily.

One of the most persistent difficulties has been that of holding the gage. In the making of 0.010-in. sheet, the original extrusion will be about 12 times this thickness or about ⅛ in. Cooling of the thick extrusion will take place only at the surface, and the rate of cooling of the plastic halfway between the top and bottom surfaces will vary inversely as the square of the thickness. Since the resistance to stretching doubles for a temperature drop of 10°, any part of the original extrusion that is thicker than the rest will be much softer and will stretch much more easily than will the initially thinner and stiffer sections when the whole has dropped to the required stretching temperature. Minor variations in the extrusion cause variations in the longitudinal thickness and also result in irregular stretching. Even now, only gages between 0.003 and 0.015 in. are regularly produced, although gages from 0.001 to 0.025 in. can be made.

Any defects are magnified, and best results were obtained only with special molding powder. After several months of cooperation on this problem with Plax Corp., Bakelite Corporation finally produced a series of excellent powders.

After the stretching, the sheet is gaged, slit, run through the puller, and is then wound into rolls. Thin Polyflex in 0.001 to 0.003 in. gage is troublesome to slit and wind because of the great static charge and extreme lightness of the sheet.

Rods up to 8 in. in diameter have been produced. Such rods require so long a cooling time and are wanted in such small quantity that they are not produced commercially in continuous extrusion. They are produced in molds filled by an extruder, and are slowly and carefully cooled.

Slabs are produced by two methods, according to size. Molten plastic is supplied from a conventional stuffer for both. In one method, a hot mold is filled and is subsequently cooled according to a definite temperature cycle so as to avoid vacuum bubbles and surface sinks.

In the other method, a special die is used, and the slab is made in continuous lengths. The die makes an extrusion with polished sur-

faces and an adjustable thickness that can be held within a few thousandths of an inch.

In the blowing process used by Plax Corp., a cylinder similar to that of an injection-molding machine is employed to force plastic through a melting zone into a special cross-feed head. It is then extruded as a tube, usually closed at the outer end. A mold is closed around the hot extrusion, and blowing air forces the soft plastic against the mold. Blowing air is usually maintained until the article has cooled sufficiently to permit removal from the mold. Only bottles made with polystyrene have been used on this machine and a few parts used for electrical equipment.

Development of the process has been slow, not because of any limitations inherent in the process, but because of the low cost of competitive products and the chemical limitations of the plastics. Glass, for example, costs about $15 per ton delivered to the forming machine, or about $0.0075 per lb., whereas the thermoplastics cost from 60 to 80 times as much.

One of the most important contributions to the war effort has been a process of treating polystyrene which permits it to be machined. Without this process, extruded products, subsequently used as machined parts, would be ineffectual because of their mechanical instability. Perhaps 90 per cent of polystyrene rods, slugs and slabs are sold for ultimate use in some kind of electronic equipment. Much of the round rod is used in automatic screw machines and semiautomatic lathes. Formerly, it was thought that polystyrene could not be machined. Several such statements occur in the literature. After an extensive study it was found that cracking is solely due to the thermal strains induced in the material. The removal of these strains is not a simple matter, and it was only after the discovery of a practicable means of evaluating the residual strains that a consistently machinable product could be produced.

Some of the difficulties involved in solving the problem may be of interest. The common method of measuring internal strain involves the use of polarized light. A relatively strain-free piece is prepared and loaded with a known load so that the resulting internal strain can be computed. Optical measurements are made which involve a

rather complicated set-up and the stress-optical coefficient is measured. Knowing the stress-optical coefficient, the residual strain, after any annealing operation (or during the annealing) can be measured. This is the standard method in studying strains in glass and some plastics. In the case of polystyrene, however, the system breaks down.

In the apparatus for measuring strain, a series of parallel lines can be seen. It is the shifting of these lines due to strain in the test piece which is measured. If there is no strain, the lines remain unchanged. Strain causes a shift to one side for tensile strains, and to the other for compressive strains. The degree of shift determines the amount and the direction of strain. Ordinarily thermal cooling strains cause a shift of only a band or two.

CHAPTER XI

New Forms and Coatings

NEW MATERIAL FORMS

In addition to the influx of new materials during recent years many new material forms have appeared. Old and new plastics alike have been fashioned in new ways to produce new effects. One of the most common methods has been the introduction of air or gas as an integral part of the new product. In this way sponge-like materials of low specific gravity have been made with several types of resins. Air bubbles have been introduced into extruded fibers. Layers of materials have been laminated to give louvered effects and ultra-thin foils and fibers have been developed.

LOUVERPLAS

Louverplas, introduced in 1940, is a louvered, laminated, cellulose acetate sheet manufactured by E. I. du Pont de Nemours & Company, Inc., for the Doane Products Corporation and distributed through Ivan T. Johnson Company, Inc.

Sheets are approximately 20 in. wide by 50 in. long and thicknesses vary from 0.04 to 0.08 in., with louver spacings ranging from 0.04 to 0.065 in. The louvers may be white, black or colored plastics and extend through the thickness of the sheet. They run only the 20-in. way of the sheet and are perpendicular to the surface with a maximum angular tolerance of 10°. The spacings between the louvers are clear, water-white, transparent plastics.

The principal use of Louverplas has been in commercial lighting, particularly in fluorescent lamps, where it is used to shield the glare. Cellulose acetate, now being used for Louverplas, is not entirely satisfactory because of its moisture absorption, high shrinkage and poor resistance to high temperatures, and a search, including some of the newer thermoplastics, is being conducted for a more suitable material.

Courtesy Ivan T. Johnson Co., Inc.

FIG. 44. Flat sheets of Louverplas will direct light rays to shield eyes of inspectors or other workers.

Louverplas will probably continue its growth in the commercial lighting field after the war, and may be reduced in price.

ETHYL CELLULOSE FILM

The Celanese Celluloid Corporation has developed a new ethyl cellulose film and foil known as Lumarith EC. This new material will be introduced after the war for use in packaging. Production is planned in thicknesses ranging from 0.001 in. to 0.0015 in.

FOAM POLYSTYRENE

Aerated polystyrene which is a sponge-like form of polystyrene is now being used in war work. The material is under strict military restrictions and no details are available as this book goes to press.

SURFACE COATINGS

These may be grouped into three main classes — varnishes, lacquers and synthetic finishes.

VARNISHES. Synthetic resins are cooked with drying oils, the resultant product then being used as a clear finish or as a pigmented enamel or undercoat. This group also includes paint vehicles in which the proportion of resin is generally small relative to the drying oil.

Types of resins used in varnishes, although available in ever-widening variety to meet individual requirements, basically were the same as in previous years. These included ester gum, alkyds, modified and unmodified phenolics, cumarone and a few other miscellaneous resins.

For many years prior to 1940 quick-drying varnishes had been based on the use of China wood oil, usually in combination with phenolic resins. But in 1940 China wood oil became very scarce and expensive and had to be replaced by other drying oils. Dehydrated castor oil was used and there was a shift in emphasis from phenolic resin to maleic alkyd types. While such varnishes do not usually air-dry as quickly as the wood oil types, they may be baked at higher temperatures because of superior retention of gloss and color and this of course cuts down the time required for drying.

LACQUERS. The vehicles in lacquers are mixtures of resin with plasticizers and cellulose nitrate or other cellulose derivatives and the film dries chiefly through evaporation of the solvent. The trend here has been toward the use of relatively large proportions of oil-modified alkyd resins in lacquers for outdoor use to obtain maximum gloss and color retention on exposure. Before the war, the use of the hard maleic alkyds in indoor lacquers was increasing, especially for the finishing of radio cabinets and furniture to which these resins imparted gloss, fullness, quick solvent release and easy rubbing properties.

SYNTHETIC FINISHES. The term "synthetic" is generally applied to those finishes in which the vehicle is predominantly a solution of synthetic resins used as such, without cooking with oil or combining with cellulose derivatives.

Among the most important members of this group are the oxidizing type alkyd resins, the use of which was rapidly increasing before the war. New resins of this type were being developed with improve-

ments in specific characteristics such as drying speed, color retention and solubility of the finishes.

Another group of resins which was showing phenomenal growth were those made from urea. These found their major application in baking enamels, usually in conjunction with alkyd resins. Such combinations bake quickly with mar-resistant hardness and excellent color retention and therefore find wide use in a variety of metal enamels.

Special urea-alkyd resin combinations were developed for certain applications such as clear wood finishes that could be baked at temperatures much lower than required by previous practice. Plasticized urea resins in emulsion form were also finding considerable use as clear finishes on paper and textiles.

MELAMINE RESINS. One of the outstanding developments in the paint industry was the commercial production in 1940 of organic soluble melamine resins. Thermosetting like the ureas, they found their chief use in baking enamels in conjunction with alkyd resins. When such combinations are baked at the temperatures normally used for the urea types, they bake more quickly and with a degree of hardness which is unusual and closely approaches molded plastics.

Melamine resins have also been found more generally satisfactory than urea types for relatively low baking schedules and they retain gloss and color to a much greater degree on prolonged subjection to high heats. They also have superior resistance to weather exposure and to grease and chemicals. With so many desirable characteristics, the melamine resins are going into enamels for use on products ranging from stoves to refrigerators and from automobiles to cake boxes.

Before the war the uses of alkyd, urea and melamine resins were being extended. These resins were finding new applications in architectural, refrigerator, washing machine, Venetian blind and sign finishes. Paints made with alkyd resin emulsion were being used for interior walls and on the exteriors of masonry buildings. Low-temperature-curing urea-formaldehyde resins were being widely adopted for furniture finishes.

The war brought many changes. Production was speeded up to meet new peak demands, production-line methods were more generally adopted for a variety of products and this put a premium on quick-drying coatings. Also, new types were needed to meet the unusually strenuous demands of military use. Concurrently, the amounts available for civilian use steadily declined. The result was an interruption of the trends which were being established before the war and also a shift in emphasis from the development of new types to new applications of those types which had already been developed.

Mandatory priorities were placed on formaldehyde and phenol and supplies of glycerin phthalic anhydride and maleic anhydride became restricted. Increasing quantities of alkyd resins were required to coat tanks, battleships and airplanes. The armed forces used larger quantities of phenolic resin varnishes and the oleoresinous finishes were used to replace or extend alkyd resin solutions.

An important development was the commercial production of faster drying oils from fish, soybean and linseed oils, and the use of such oils in quick-drying varnishes. Extensive investigations were made upon methods for producing fast-drying water-resistant varnishes without the use of China wood oil. By processing high-viscosity phenolic resins, varnishes were obtained having satisfactory drying combined with water and alkali resistance. Many new oils were introduced for use in place of phenolic resins and China wood oil to give satisfactory fast-drying coatings.

New Coating Materials. It is reasonable to expect that the alkyd and urea resins, which were showing so many promising new applications in surface coatings before the war, will resume their upward trend after the cessation of hostilities. This is particularly true since new types of these materials have been developed.

The new alkyd resins discussed in Chapter II are considered to have unusual possibilities in surface coatings.

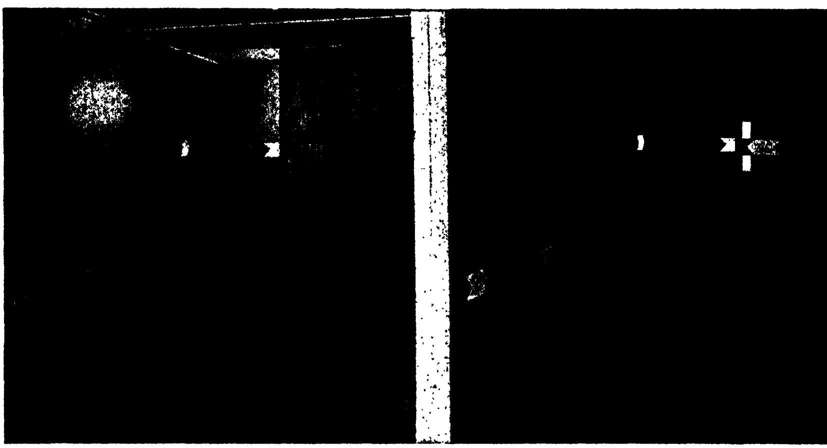
Radically new types of urea paints have also been developed. One is said to dry in 10 min. and to have unusual possibilities for hotel rooms, hospitals and other buildings where paints with extremely short drying time are required. Another new type of urea paint is

said to be fire resistant and to have been used successfully in Great Britain to prevent spread of fires caused by incendiary bombs.

Many of the new materials discussed elsewhere in this book will undoubtedly find important applications in the field of surface coatings. Companies engaged in making paints and other surface coatings are carrying on extensive research with the new materials but the results are not yet available.

LUMINESCENT PIGMENTS

Luminescent pigments may have an important effect on the use of plastics. They have the ability to absorb radiant energy from a light source and, after converting that energy to another form, to re-emit it as a visible, colored light. The pigment swallows up one



Courtesy The New Jersey Zinc Co.

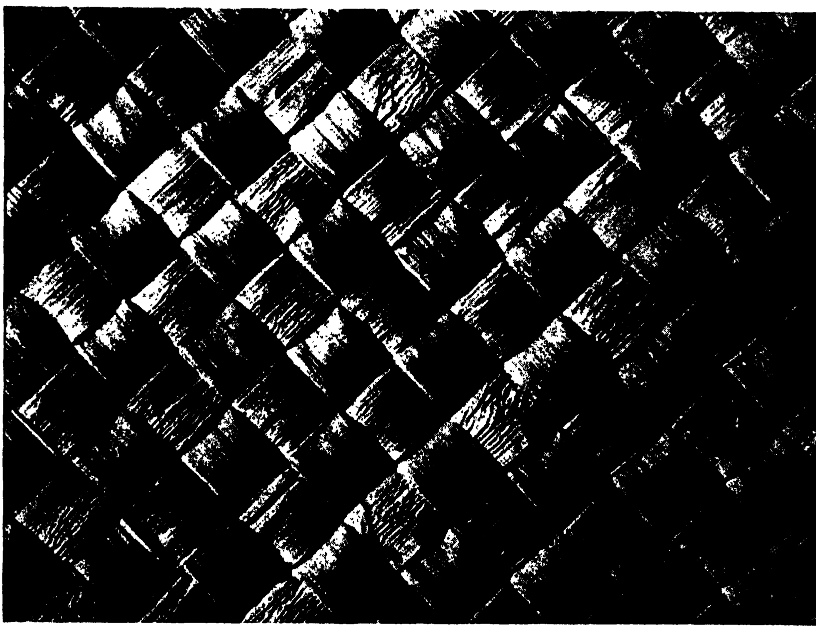
FIG. 45. By use of spots of luminescent paint, people may be guided in the dark. This might be important in schools and theaters. Spots need not show in daytime. At right, lights in scene at left have all been extinguished.

form of light and, immediately or slowly, re-emits visible light of a different color. A wide range of luminescent colors can be developed by variation in the manufacturing process.

Luminescent pigments are of two types — phosphorescent and fluorescent. A phosphorescent material continues to glow after the exciting light is removed or extinguished. A fluorescent material

glows only during the time that the pigment is exposed to outside excitation.

The New Jersey Zinc Company, Sylvania Electric Products, Inc., and General Luminescent Corp. have done considerable work in the development of these luminescent pigments. Phosphorescent pigments have, of course, been known for a long time and have found



Courtesy The New Jersey Zinc Co.

FIG. 46. This shows fabric woven with some of the strips made of luminescent material. As a wall covering or for stage use it shows interesting patterns in the dark.

important military applications during the war. The principal improvement in this class of materials has been an increase in their luminosity and thus an extension of the time of afterglow. The fluorescent pigments have been developed more recently, and during the last few years a full line has been introduced.

Luminescent pigments should find important postwar applications, particularly in conjunction with plastics, with which they

may be used in several ways. They may be incorporated in transparent or translucent plastics at the mill. Finished plastics articles may be coated with luminescent paint, or designs and decorations may be printed on the article through the use of luminescent inks. Decalcomanias offer another interesting, inexpensive possibility.

Luminescent plastics may be used for such applications as luminescent electric lamp shades, light transmitters, product name plates on all kinds of consumer goods, compacts, cigarette cases and lighters, cosmetic jars, dresser sets, costume jewelry, belt and shoe buckles, ash trays, vases, lamp bases, light switch plates, Christmas tree ornaments and decorations and innumerable other items. Textile fabrics may be coated or printed with luminescent pigments for such applications as marking tapes, draperies, upholstery, and wall and floor coverings.

Among the companies interested in the use of luminescent pigments in plastics are Monsanto Chemical Company, Nixon Nitration Works and Manufacturers Chemical Company.

CHAPTER XII

Plastics Trends

The plastics output in 1941 was approximately 500,000,000 lb. compared with less than 50,000,000 lb. in 1931, a tenfold increase.

Production of coal-tar resins, according to government data, was under 2,000,000 lb. in 1921, but by 1931 it had increased to 34,000,000 lb., and by 1941 to over 343,000,000 lb. The growth of these resins in recent years has paralleled that of the total plastics industry.

Sheets, rods and tubes of cellulose nitrate, the earliest of the modern plastics, declined from about 17,500,000 lb. in 1929 to 16,500,000 lb. in 1941, largely because it was supplanted by acetates and vinyls in manufacture of automobile safety glass, formerly one of its largest markets.

The production of cellulose acetate sheets, rods and tubes increased with its wider use for safety glass from about 2,500,000 lb. in 1933 to over 13,000,000 lb. in 1937. In recent years vinyl resins have displaced the acetates in safety glass with accompanying temporary drop in acetate output.

Production of cellulose acetate molding powder, however, has grown from around 7,000,000 lb. in 1938 to nearly 31,000,000 lb. in 1941.

The most spectacular expansion has occurred in the non-coal-tar synthetic resins. Production of less than 2,000,000 lb. in 1932 had risen to over 94,000,000 lb. by 1941 and to 248,000,000 lb. by 1943. The non-coal-tar resins include among others the ureas, vinyls and acrylics which have been among the most rapidly growing of all individual types of plastics.

The output of urea resins, around 3,000,000 lb. in 1933, had reached almost 35,000,000 lb. by 1941 and 54,000,000 lb. by 1943. Although comparable production data are not available for the vinyl and acrylic resins, their growth has been rapid.

PRICES. There has been a gradual and substantial reduction in plastics prices. The price of the coal-tar synthetic resins in 1921 was \$0.81 per lb. and by 1941 had dropped to \$0.26. Parallel trends have been evident in other important groups of plastics. For example, the price per pound of the ureas dropped from \$0.48 in 1933 to \$0.32 in 1941.

This general downtrend of prices has been characteristic of the entire synthetic chemical industry and has been an important factor in the displacement of natural materials by synthetic materials. It reflects not only the development of new and improved processes, but also the utilization of cheaper raw materials and the application of mass-production methods.

EFFECTS OF WAR ON THE PLASTICS INDUSTRY. Plastics production when the war started was at a peacetime high, and yet output had to be stepped up sharply to meet wartime demand.

The expansion of productive capacity for styrene, acrylic and vinyl resins has been particularly marked. In order to meet our synthetic rubber program, we have developed a capacity of 400,000,000 lb. of monomeric styrene a year. Productive capacity for phenol-formaldehyde, acetylene, alcohol and a number of other vital chemicals has also been increased enormously during the war period. Such new materials as the silicones, polyethylene, tetrafluorethylene, the newer melamines, the allyls, the furfurals and others in new peacetime applications undoubtedly will further boost total output for the industry.

New processes have also come into the picture to help speed war production. One of the most important of these is electronic preheating in molding, which will greatly increase the applications of the thermosetting resins by lowering costs and increasing molding size, thus widening the range of new products.

The wide use of plastics in the aircraft and other war industries has helped to switch the industry from the decorative arts to carefully engineered products. This has emphasized scientific methods of production and more careful attention to tolerances. The result may well be a permanent change in plastics markets.

The urgent call for plastics as substitutes for high priority metals

early in the war resulted in many new applications, some of which will remain even after the older materials are again available, for despite some failures many of the war applications of plastics have been surprisingly satisfactory.

PLASTICS IN THE POSTWAR PERIOD. Probably the most important single factor in appraising the postwar outlook for plastics is the vast expansion in productive capacity already referred to.

After the abnormal war demand is lifted, productive capacity almost certainly will be excessive for a time. Therefore price trends will be downward in an attempt to take up the slack. This will improve the competitive position of plastics relative to other materials and will result in new applications and a broader market.

Plastics already have a foothold in virtually every industry, but they account for a relatively small proportion of the total volume of materials used and therefore have a wide opportunity for growth.

The automobile industry is typical. The prewar car weighed about 1½ tons but had only about 5 lb. of plastics in it. The postwar car is expected to use a minimum of 15 or 20 lb. of plastics. Although this is small in comparison with the total amount of all materials used, it represents an increase of 200 or 300 per cent compared with prewar use. The output of automobiles in the postwar period is estimated at over 5,000,000 a year, which means the prospect of from 75,000,000 to 100,000,000 lb. of plastics annually.

Another large volume industry in which plastics should find greatly increased use is building. An all-plastics house is just about as unlikely as an all-plastics automobile, but the use of plastics in the industry should show a tremendous increase from its prewar level. Plastics cannot compete on a price basis with conventional building materials, but they will be used in bonding plywood, which will undoubtedly come into wider use as a basic material, and will have many other applications in the building industry. Lewis H. Brown, president of Johns-Manville Corporation, recently stated that the building industry is interested in the use of plastics and is only waiting for a low cost material. He expressed the opinion that such a material might be made available within the next ten years.

Plastics fabricators now serving the aircraft industry should be especially alert for new markets because of the expected contraction of aircraft production after the war.

Effects on Other Materials. Plastics will affect other materials in two principal ways: (1) through displacement as the result of competition and (2) through the use of new combinations of plastics with other materials. Probably the second will be far more important than the first.

Plastics will not be important as a competitive threat to the large-volume, low-cost materials such as wood, steel, cement, brick, stone and glass. The output of steel before the war, for instance, measured on a weight basis was about 250 times that of plastics.

Plastics will compete, however, with various special-purpose materials such as silk, tin for coating purposes, and other materials that may be largely displaced in important markets.

Plastics combine readily with other materials and will be used with them to an increasing extent. The new plastics adhesives, which join such widely different materials as wood, metals and rubber, will have a significant role in the future combining of materials that differ in function.

The designer of products will have a much wider selection of suitable materials for each particular job than he ever had before.

Perhaps the main threat of plastics will be not to other basic types of materials, but rather to those designers of products who fail to utilize plastics. Those who do not know plastics and thus do not use them where best design indicates their use are certain to be left behind in the coming struggle toward a higher standard of living.

Outlook for Individual Types of Plastics. As new plastics come into the picture some of the older types will be crowded out of their established markets.

It is generally conceded that the vinyls, styrenes, acrylics and some of the newer types will probably have the biggest growth in the postwar years, because productive capacity has been greatly expanded to meet war demand.

For example, styrene capacity has been enlarged in connection with the synthetic rubber program and new markets for it will be needed after the war. Polystyrene may drop to $0.20 per lb. or even

to $0.15, and the resulting wider use may make polystyrene the principal material for injection molding in this country, as it was before the war in Europe.

Polystyrene and the vinyls will have a stronger competitive position in relation to cellulose acetate in injection molding. Many expect the cellulose group of plastics as a whole to lose ground, although ethyl cellulose and some of the other newer types may continue to show growth because of their special properties.

The melamines will probably displace the ureas in some markets. The melamines have been found to have better properties than the ureas for some war applications. In the future peacetime market the melamines may become the ideal material for tableware. They may also come into the plywood picture because they resist heat and moisture better than the ureas. Much, however, will depend upon relative prices.

Nylon molding powder is expected to have a particularly bright future if its price can be reduced sufficiently. Many molders have done work with nylon and are satisfied with results.

Some of the other new types of plastics undoubtedly will have bright futures.

Research and the Future. One of the most impressive things about plastics is the large number and variety of companies and industries which are interested in them. In a narrow sense, plastics might be regarded as a subdivision of the chemical industry, but in a broad sense, the term includes not only the manufacture of materials, which is a chemical operation, but the fabrication and use of these materials, which encompasses a great number of other industries.

For example, the steel industry is much interested in plastics not as a possible threat to steel, but from the standpoint of affording a stimulus to steel application. The demand for steel merely to make molding and fabricating equipment should exceed its displacement by plastics. Plastics will be used in combination with steel for machine tools, gears, cams, protective coatings and the like. If 1 lb. of plastics could be used with every 100 lb. of steel, the demand for this purpose alone would nearly double the plastics output.

The glass companies also are much interested in plastics. Here

again the competitive threat will probably not be important except in certain special applications. Glass is so cheap relative to plastics that plastics cannot very well compete for window glass or milk bottles. But some of the newer transparent plastics such as the allyl resins may invade the safety glass market and other specialized glass applications.

The big rubber companies are doing much research on plastics, as well as on synthetic rubbers. The elastic vinyls and other elastomers have been widely used as rubber substitutes during the war, and will probably take over some of the prewar uses of rubber permanently. The dividing line between synthetic rubber and plastics is becoming more nebulous and it is only natural that there will be many borderline markets which can use either type of material.

The new plastics may revolutionize the wood and paper industries and it is not surprising that the companies in these fields are much interested. The use of plastics has not only enabled lumber to stage a comeback in the form of greatly improved plywood, but has increased the potential uses of paper and pulp. These industries appear to have everything to gain and nothing to lose by the coming of plastics.

Not only are the large producers of all the basic types of materials much interested in plastics, but the leading consumers of such materials are also following developments closely. For example, the automobile companies have special research divisions to investigate possible new applications and predict that more plastics as well as more light metals will be used in the postwar car, even though steel continues as the basic structural material.

The Bell Telephone Laboratories, largest research laboratory in the world, has a special plastics division and expects to use much more plastics material after the war in manufacture of telephone apparatus.

There were in all around 150 companies engaged in special research in the field of plastics in 1940, according to a Bulletin of the National Research Council. These companies included not only chemical producers, but practically all kinds of companies producing or using plastics materials. With such wide range of

study, new developments are bound to occur in almost every direction.

In general, the objectives of such research fall into the following broad classes:

(1) Improvements in known materials to extend their use and field of application.
(2) Development of entirely new types of materials.
(3) Reduction in costs of production through process improvements.
(4) Utilization of waste materials.

It is reasonable to expect that marked progress will occur in all these directions in the postwar years. The number of types of possible plastics is almost unlimited. For example, the number of types of nylon theoretically possible runs into the thousands while only 11 different types are now being produced. Many of these new materials will of course not prove feasible, but the illustration serves to give some idea of the vast number of chemical combinations possible.

An attempt will also be made to utilize a much greater range of raw materials, particularly agricultural waste materials. Intensive efforts have already occurred in the cases of such chemurgic materials as sugar cane, wood waste and skimmed milk. Many believe, however, that the plastics made from chemurgic materials are not as promising as those made from coal, petroleum and other standard chemical raw materials.

Some Broad Implications. The plastics industry must be regarded as one of our most promising, if not our most promising growing industry. It should help to take up some of the slack in postwar employment, offer a new outlet for surplus investment funds, generally stimulate business activity and eventually contribute to higher standards of living.

The industry has a big job to do in the field of education. This consists not only in helping to provide technical training for those engaged in production and fabrication, but involves considerable publicity work as well. Perhaps the public has been led to expect

too much from plastics in the immediate postwar years, and rapid as has been the growth of the industry, it will be many years, if ever, before it reaches maturity. Therefore the industry should discourage exaggerated expectations on the part of the public as regards the immediate postwar years. This will require considerable publicity and education. As many in the industry have also pointed out, the public should be taught to distinguish between different types of plastics. Otherwise the wrong application of a particular type may reflect on the industry as a whole. The public can distinguish between different types of metals, and it must also distinguish between different types of plastics. This may require not only labeling of the different products, but also educating the public as to their advantages and limitations.

The following tabulation, showing the estimated 1944 production of plastics in millions of pounds, is based upon the paper read before the Cleveland meeting of the American Chemical Society, April 5, 1944, by Dr. Gordon M. Kline.

Material	1944*	1943	1940
Cellulose Compounds			
Nitrates	20	20	12
Acetates	55	55	24
Acetate butyrates	34	32	8
Acetate propionates	34	32	8
Ethyl cellulose	34	32	8
Thermoplastics Resins			
Polystyrenes	4	4	2
Methyl methacrylates	50	37	3
Polyvinyls	108	83	18
Cumarone-indene, etc.	55	55	26
Alkyds	100	100	100
Thermosetting Resins			
Phenolics	176	152	93
Ureas	75	65	22
Totals	677	603	308

* Estimated.

PRODUCTION OF PLASTICS AND RESINS

(thousands of pounds)

General Classes

	Cellulose Nitrate Sheets, Rods and Tubes	Cellulose Acetate		Synthetic Coal-Tar Resins	Non-Coal-Tar Resins
		Sheets, Rods and Tubes	Molding Powder		
1943				403,649	247,862
1942	N.R.	N.R.	N.R.	291,606	135,125
1941	16,499	6,218	30,717	343,675	94,125
1940	11,915	8,887	14,963	222,943	53,871
1939	13,373	9,140	11,655	179,338	33,690
1938	9,488	6,831	7,394	106,923	23,435
1937	17,722	13,235	N.R.	142,025	21,006
1936	16,935	13,036		117,302	15,611
1935	16,205	10,504		90,913	Est. 10,000
1934	12,360	4,826		56,059	Est. 5,000
1933	11,916	2,482		41,628	3,572
1932	Est. 9,300	N.R.		29,039	1,898
1931	Est. 12,300			34,179	N.R.
1930	Est. 12,300			30,868	
1929	Est. 17,500			33,036	
1928				20,411	
1927				13,452	
1926				N.R.	
1925				N.R.	
1924				N.R.	
1923				N.R.	
1922				5,944	
1921				1,644	

PRODUCTION OF PLASTICS AND RESINS

(thousands of pounds)

Individual Types

	Tar-Acid Resins (Phenolics)	Urea Resins	Alkyd Resins
1943	164,308	53,859	(a) 179,188
1942	147,188	37,516	(a) 98,998
1941	156,628	34,849	(a) 137,837
1940	93,434	21,492	(a) 97,923
1939	66,684	16,569	(a) 76,472
1938	43,964	8,250	(a) 40,997
1937	80,771	N.R.	(a) 61,254
1936	70,350	N.R.	(a) 46,952
1935	52,977	4,203	34,313
1934	40,664	3,471	15,219
1933	31,698	3,234	9,931
1932	17,163		
1931	22,647		
1930	18,338		
1929	26,236		

NOTES

N.R. = Not Reported.

The data on cellulose nitrate and cellulose acetate are based on U. S. Department of Commerce reports.

The data on synthetic resins which include among others the phenolic, urea and alkyd resins are based on U. S. Tariff Commission reports.

Production of dried casein has been compiled by the U. S. Department of Agriculture.

(a) Includes resins from maleic anhydride.

PRICES OF PLASTICS AND SYNTHETIC RESINS

(Unit Value per Pound)

	Groups		Types		
	Synthetic Coal-Tar	Non-Coal-Tar Resins	Phenolic	Alkyd Resins	Urea Resins
1943	$0.22	$0.47	$0.32	$0.19	$0.26
1942	0.30	0.57	0.30	0.22	0.31
1941	0.26	0.55	0.26	0.20	0.32
1940	0.22	0.55	0.28	0.18	0.39
1939	0.18	0.46	0.18	0.21	0.36
1938	0.19	0.41	0.20	0.20	0.44
1937	0.19	0.30	0.18	0.20	N.R.
1936	0.20	0.24	0.19	0.22	N.R.
1935	0.19	N.R.	0.19	0.22	0.46
1934	0.23	0.43	0.26	0.14	0.41
1933	0.23	0.54	0.25	0.18	0.48
1932	0.21	0.45			
1931	0.27				
1930	0.30				
1929	0.33				
1928	0.35				
1927	0.47				
1926	N.R.				
1925	N.R.				
1924	N.R.				
1923	N.R.				
1922	0.67				
1921	0.81				

Note: N.R. = Not Reported.

Source: U. S. Tariff Commission.

PLASTICS SALES FOR 1940

(Estimated)

American Cyanamid Co.	$ 7,000,000
E. I. du Pont de Nemours & Co., Inc.	25,000,000
Eastman Kodak Co.	6,000,000
General Electric Co.	9,000,000
Hercules Powder Co.	3,800,000
Monsanto Chemical Co.	10,000,000
Plaskon Division	7,500,000
Union Carbide & Carbon Corp.	20,000,000

1941 CONSUMPTION OF PLASTICS ACCORDING TO PROCESSES

Process	*Lb.* $\times 10^6$
Bonding (Adhesive)	35
Casting	7
Coatings (Paint)	125
Extrusion	12
Molding	105
Rolled Plastics (Interleaving for Safety Glass)	15
	299

COMPARATIVE COSTS

Material	Estimated Present Capacity of Production, Short Tons	Equal Volume Basis, Cu Ft	Cost per Cu Ft
Aluminum	1,100,000	13,000,000	$25.00
Copper	1,100,000	4,000,000	85.00
Magnesium	300,000	5,600,000	22.00
Plastics	400,000	9,800,000	36.00 (Average all Plastics)

COST OF SPECIFIC PLASTICS MATERIALS

Material	Cost per Lb	Cost per Cu Ft
Acetate	$0.45	$37.00
Acrylates	0.85	69.00
Nitrates	0.45	39.00
Phenolics	0.14	12.00
Polystyrene	0.35	23.00
Ureas	0.32	30.00
Vinyls	0.48	38.00

COMPARISON OF PLASTICS WITH OTHER CONSTRUCTION MATERIALS

Specific Gravity		Tensile Strength, psi		Modulus of Elasticity, psi	
Lead	11.34	Alloy steel	189,000	Alloy steel	30×10^6
Copper	8.89	K Monel	185,000	Structural steel	30×10^6
Phosphor bronze	8.81	Phosphor bronze	120,000	K Monel	26×10^6
K Monel	8.80	Nickel silver	108,500	Nickel silver	20×10^6
Nickel silver	8.68	Structural steel	85,000	Copper	16×10^6
Structural steel	7.85	Duralumin	55,000	Phosphor bronze	15×10^6
Alloy steel	7.80	Nylon	50,000	Zinc die cast	13×10^6
Zinc	7.14	Copper	47,000	Zinc	12×10^6
Zinc die cast	6.60	Zinc die cast	35,000	Duralumin	10×10^6
Aluminum die cast	2.90	Aluminum die cast	29,000	Aluminum	10×10^6
Duralumin	2.79	Aluminum	22,000	Aluminum die cast	10×10^6
Aluminum	2.70	Zinc	17,500	Glass	9×10^6
Glass	2.60	Wood	16,000	Lead	2.5×10^6
Concrete	2.31	Plywood	9,600	Concrete	2×10^6
Lignin fiber	1.45	Glass	9,500	Plywood	20×10^5
Phenolic plastic	1.38	Lignin fiber	9,500	Wood	18×10^5
Cellulose acetate	1.32	Phenolic plastic	7,500	Lignin fiber	17.5×10^5
Hard rubber	1.30	Hard rubber	7,000	Phenolic plastic	12.5×10^5
Cellulose acetate butyrate	1.28	Polystyrene	7,000	Methyl methacrylate	5×10^5
Methyl methacrylate	1.18	Cellulose acetate	6,700	Polystyrene	4.5×10^5
Nylon	1.14	Cellulose acetate butyrate	5,000	Nylon	4.5×10^5
Polystyrene	1.06	Methyl methacrylate	5,000	Hard rubber	3×10^5
Plywood	0.68	Lead	2,700	Cellulose acetate butyrate	2.7×10^5
Wood	0.63	Concrete	200	Cellulose acetate	2.7×10^5

Source: J. R. Townsend, Bell Telephone Laboratories.

RATIO OF TENSILE STRENGTH TO SPECIFIC GRAVITY

Nylon	43,860	Lignin laminate	6,550
Wood	25,400	Phenolic plastic	5,430
Alloy steel	24,230	Hard rubber	5,380
K Monel	21,020	Zinc die cast	5,300
Duralumin	19,710	Copper	5,290
Plywood	14,120	Cellulose acetate	5,080
Phosphor bronze	13,620	Methyl methacrylate	4,240
Nickel silver	12,500	Cellulose acetate butyrate	3,910
Structural steel	10,830	Glass	5,850
Aluminum die cast	10,000	Zinc	2,450
Aluminum	8,150	Lead	240
Polystyrene	6,600	Concrete	90

Source: J. R. Townsend, Bell Telephone Laboratories.

ELECTRICAL PROPERTIES OF PLASTICS MATERIALS

Material	*Loss Factor* (K × PF%) 10^6 *Cycles*	*Material*	*Dielectric Constant* 10^6 *Cycles*
Urea-formaldehyde	18	Urea-formaldehyde	6.6
Phenol plastic	16	Phenolic laminate	5.0
Vinylidene chloride	12	Phenolic plastic	4.5
Cellulose acetate	11	Shellac	4.4
Cellulose acetate butyrate	11	Vinylidene chloride	4.0
Nylon	10	Cellulose acetate	3.6
Phenolic fiber	10	Cellulose acetate butyrate	3.6
Shellac	9	Nylon	3.4
Vinyl chloracetate	6	Aniline formaldehyde	3.3
Methyl methacrylate	6	Vinyl chloracetate	3.3
Aniline formaldehyde	2	Methyl methacrylate	3.0
Hard rubber	1	Hard rubber	3.0
Polystyrene	0.05	Polystyrene	2.6

Source: J. R. Townsend, Bell Telephone Laboratories.

PHYSICAL AND MECHANICAL PROPERTIES OF IMPACT-GRADE MOLDING MATERIALS

Molding Compounds	Phenolic, cord-filled	Phenolic, fabric-filled	Melamine, fabric-filled	Phenolic, wood-flour-filled
Particle size	Cut cord	Macerated fabric	Macerated fabric	Passes U. S. Std. 16-mesh screen
Apparent Density, g/cc	0.18–0.20	0.10–0.13	0.10–0.13	0.52–0.58
Compression Ratio	6.5–7.5	10.5–11.5	10.5–11.5	2.3–2.6
Flow	Medium hard	Medium hard	Medium hard	Soft, medium hard
Specific gravity, g/cc, 25°C	1.35–1.38	1.35–1.38	1.50	1.35–1.38
Specific volume, cu in/lb, 25°C	20.0–20.5	20.0–20.5		20.0–20.5
Shrinkage, in./in.	0.003–0.005	0.004–0.006	0.004–0.006	0.005–0.007
Water absorption, %, ASTM D570–40T, 48 hr, 25°C	1.0–1.5	1.0–1.5	0.8–1.5	0.5–1.0
Dielectric strength, short time, v/mil, ASTM D150–39T, ⅛-in. specimen, condition 96 hr, 70% humidity, 25°C	300–450	300–450	300–400	300–400
Ultimate flexural strength, lb/sq in., ASTM D48–39	13,000–14,000	11,000–12,000	13,000–14,000	9,000–10,000
Deflection at break in flexure, in., ½ in. × ½ in. × 5 in. specimen, 4 in. span	0.095	0.075	0.063	0.065
Ultimate tensile strength, lb/sq in., ASTM D638–41T	6,500–7,000	6,500–7,000	6,500–7,000	6,500–7,000
Impact strength, Izod, ft-lb/in. of notch, ASTM, D256–38	7.5–8.0	2.8–3.2	1.0–2.0	0.28–0.32

Specimens were conditioned according to paragraph 4a of ASTM, D570–40T, and a 48-hr immersion period was used instead of the 24-hr immersion period specified by the ASTM method.

Source: Product Engineering.

OUTSTANDING PROPERTIES OF SOME NEW PLASTICS

Material	Customary Classifications	Forms Available	Typical Trade Names	Outstanding Properties
Vinylidene chloride . . .		Molding powder, stock rods, tubes, films	Saran	High tensile strength, water and chemical resistance, crystalline structure, good moldability for heavy sections
Nylon		Molding powder, filaments	Nylon	Improved heat resistance, high tensile strength, limited moldability
Polyvinyl alcohol		Molding powder, sheets, films	PVA Resistoflex	Chemical resistance plus flexibility
		Thermosetting		
Melamine-formaldehyde	General purpose Alpha-cellulose filler	Molding powder	Catalin Melamine Melmac Plaskon Melamine	High arc resistance and dielectric strength, chemical inertness, available in white and colors, good abrasion resistance
	Impact material Fabric-filled			
	Heat resistant Mineral-filled			
	Industrial and decorative laminates with paper and cloth filler	Laminated sheet, rods, tubes		
Allyl resins		Custom castings; stock sheets, rods, tubes; laminated shapes, sheets, rods	CR-39	Clear transparent, high heat distortion, hardness and abrasion resistance

Source: Product Engineering.

RECENT NEW DEVELOPMENTS

There are many new developments in the field of plastics to be announced in the near future which cannot be publicized yet. Some developments released too late for inclusion in the body of this book are described briefly here.

DIAPLEX

Films made of Bentonite, a natural clay of very fine particle size, have been modified and greatly improved and are available now under the trade name of Diaplex. The improvements result from careful purification of materials, process control, and incorporation of a small amount of a suitable resin to act as a binder, plasticizer and water repellent.

Diaplex has been suggested as a dielectric for stacked capacitors and for other electrical insulating applications. It is manufactured in film thickness of 0.0010 to 0.0017 in. The following table lists some of the properties given by the manufacturer (Rohm & Haas):

PROPERTIES OF DIAPLEX 10

Specific gravity	1.8–1.9	
Dielectric constant	4.7–4.8	
Dielectric strength, volts/mil, AC	4000	
Power factor		
	25°C	100°C
1 kc	0.35%	0.45%
1 mc	0.30%	0.40%
Thermal stability	Good	
Stable at temperatures as high as 250°C for several days.		

SILICONE RUBBER

Silicone rubber, recently announced by General Electric, retains its elastic properties at temperatures as low as 60° below zero or as high as 575°F.

One of its uses is in a gasket for the turbosuperchargers on B-29 superfortresses, where natural rubber will not provide the required resiliency for protracted periods. A synthetic rubber that was tried

became hard and brittle after 100 hours' operation at 300°F. In contrast, a gasket of silicone rubber is still soft after operating continuously for 150 hours. Silicone rubber can be compressed to two-thirds its thickness at 300°F. for several hours and will return when released to 90 per cent of its former dimensions.

Another important application of silicone rubber is in shock mountings for Navy searchlights to prevent breakage of glass during gun blast. Only silicone rubber combines the desired resiliency and heat resistance.

The raw materials from which silicone is prepared are easily available, and it can be prepared in a wide variety of physical properties.

In one form it appears much like taffy candy but can be handled without stickiness and can be rolled into a ball and bounced. This variety has been called bouncing putty and has possibilities for golf ball centers and similar applications.

LIGNOLITE 110

A new laminated lignin plastic produced by Marathon Corporation is called Lignolite 110. It is strong, lightweight, uniformly dense, and resistant to water, oil, grease and dilute acids. It has high mechanical strength and excellent electrical properties and is easily fabricated.

It is made by bonding together lignin-enriched cellulose fibers with heat and pressure. It is supplied in natural black color with a satin or sandblast finish and is available in thicknesses from $\frac{1}{64}$ to 2 in. Standard sheets are 46 by 46 in.

The specific gravity is approximately 1.4, and its weight is estimated at 20 cu. in. per lb.

Lignolite 110 is not recommended for use at over 158°F. because it tends to blister and delaminate above that temperature. The material has good resistance to warpage and can be painted, sawed, turned, drilled, tapped, threaded, milled, and punched.

DOW STYROFOAM

A new feather-weight sponge-like material has been announced by Dow and has been given the descriptive name foam polystyrene.

The following are representative physical properties:

Density, lb/sq in.	1.0–2.0
Compression strength, lb/sq in.	5–20
Modulus of compression, lb/sq in.	270–1100
Modulus of elasticity in bending, lb/sq in.	520–2000
Tensile strength, lb/sq in.	20–40
Impact strength, in.-lb (3/8 by 1/2-in. specimen)	0.3–0.6
Dielectric constant	1.00+ at 1000 cycles
Power factor, %	0.002+ at 1000 cycles
Low thermal conductivity	
Low moisture absorption	

Foam polystyrene retains its physical characteristics over long periods at a temperature of 175°F. and is reasonably stable for shorter periods up to 190°F. It burns slowly and can be ignited only over an open flame. It is easily workable and may be bonded successfully to wood, metal and other materials as well as to itself through the use of adhesives and cements.

Dow now has the material in limited commercial production. Possible applications include giving buoyancy to boats and life rafts and use in the insulation field for cold, sound and electrical insulation.

MONSANTO THALID X-500 RESINS

Monsanto now produces a new low-pressure laminating material called Thalid which is a completely reactive thermosetting resin. With Thalid as the glue, laminates of wood veneer, sheet metal, or similar materials can be cheaply and quickly formed.

When the filler material is Fiberglas cloth a tensile strength close to 50,000 lb. per sq. in. can be secured.

The resin is basically clear transparent with a slight amber cast. Colorants can be incorporated to produce a wide range of colors.

The weight of the finished product depends on the filler used. Laminates with Fiberglas have a specific gravity of approximately 1.75. Specific gravities as low as 1.35 are possible with other fillers.

Airplane parts made of Thalid have shown excellent weather resistance. Strength is maintained at extremely low and extremely high temperatures.

The fully cured laminates are free from noticeable taste or odor, are resistant to solvents and chemical agents other than strong alkalies, and have excellent insulating properties.

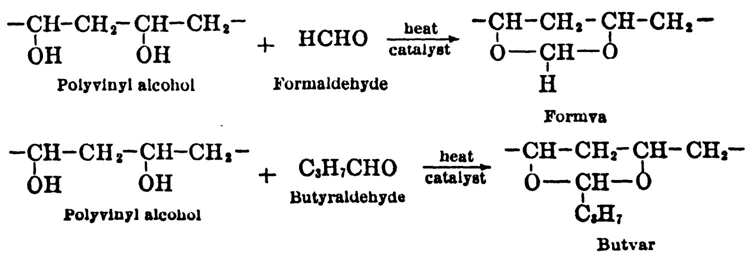
Heat resistance varies with the filler. Service temperatures as high as 275°F. are feasible.

Applications in the future may include wall panels, furniture, cabinets and housings, toys, luggage, aircraft parts, automobile parts, and perhaps packaging.

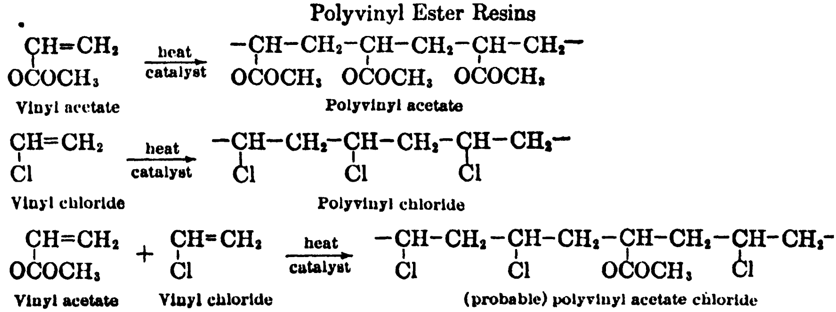
APPENDIX

The following formulas covering most of the new plastics have been prepared from the latest available data. They are presented here for reference in order to avoid including such technical material in the body of the book.

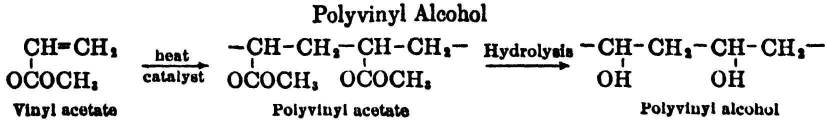
Formva and Butvar Resins



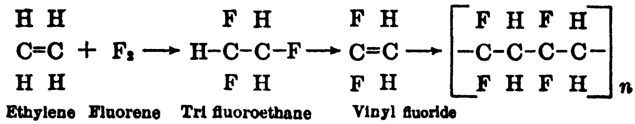
Polyvinyl Ester Resins



Polyvinyl Alcohol

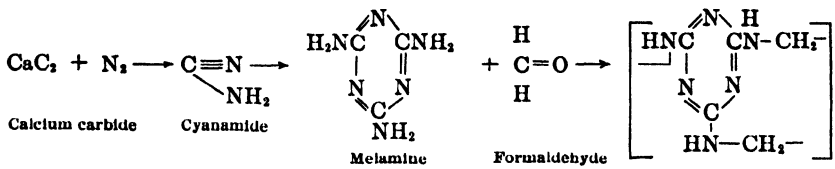


Tetra fluoroethylene Resin

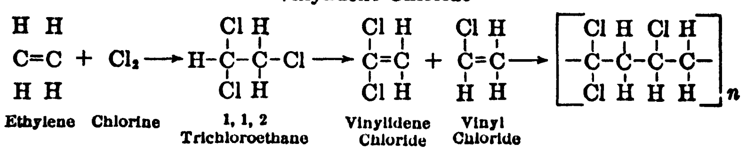


Probable reaction

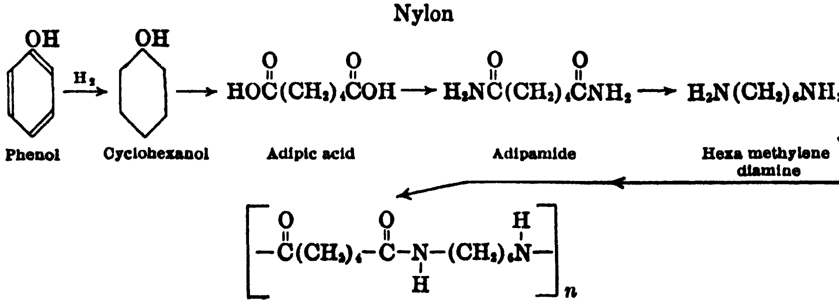
Melamine



Vinylidene Chloride

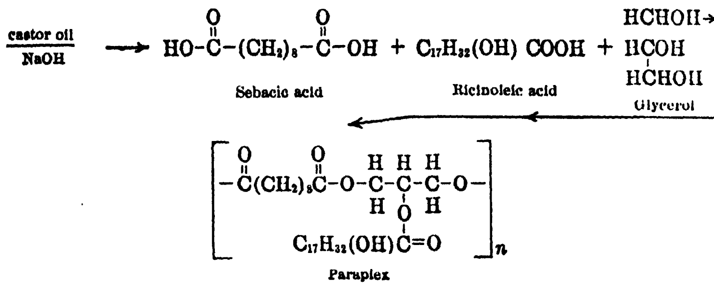


Nylon

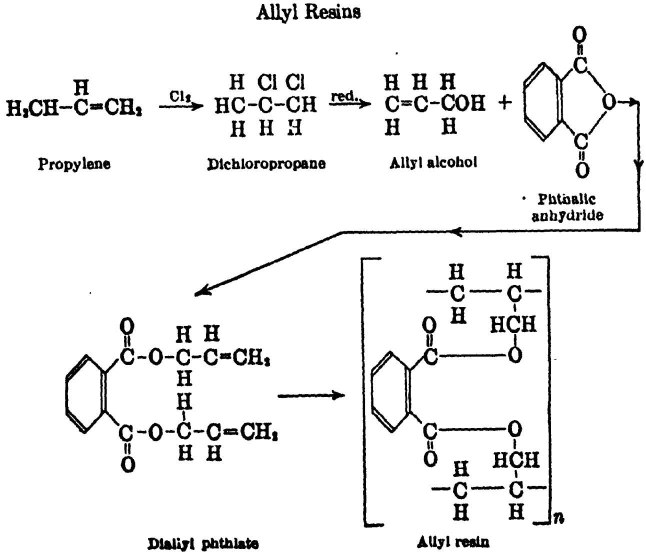


Nylon

Paraplex



Allyl Resins



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